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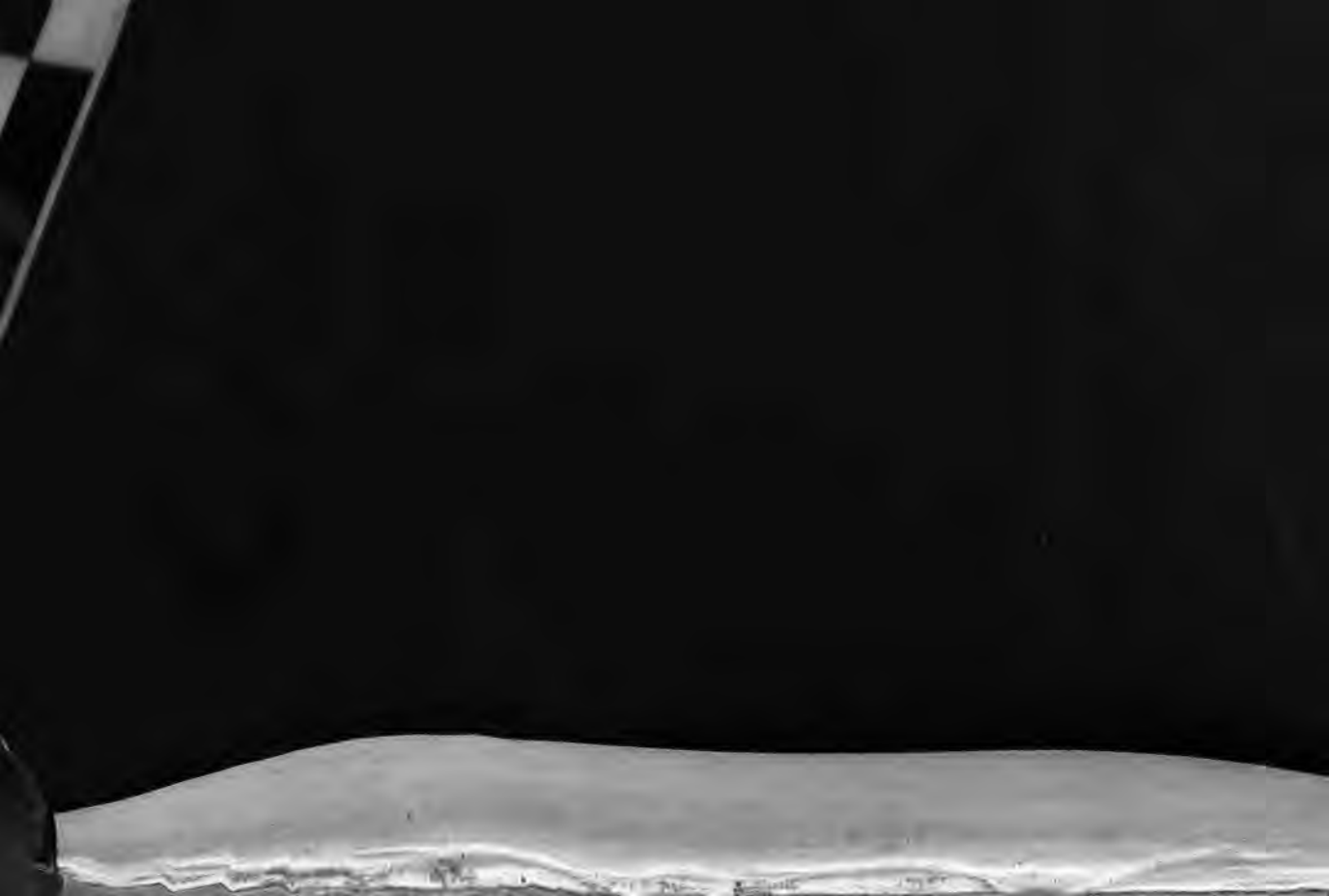

LABORATORY EXERCISES

IN

PHYSICAL CHEMISTRY.

BY

FREDERICK H. GETMAN, PH.D.,

Fellow by Courtesy of The Johns Hopkins University,
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FIRST EDITION.

FIRST THOUSAND.

NEW YORK:
JOHN WILEY & SONS.
LONDON: CHAPMAN & HALL, LIMITED
1904.

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ROBERT DRUMMOND, PRINTER, NEW YORK.

PREFACE.

With the growth of a new science between physics and chemistry there has arisen need for a new type of laboratory manual. This need has been met by two books—Ostwald's "Physiko-Chemische Messungen" and Traube's "Physikalisch-Chemische Methode." Notwithstanding the excellence of these books they have not proven themselves practical guides in the laboratory, owing to too great detail and too many references to the literature. With the wish to prepare a manual which may be placed in the hands of the student of physical chemistry, the author has written this book. He would state at the outset that he in no way considers this as an effort to rival either of the above books, which for long must remain the standard works of reference on physico-chemical measurements. The effort has been made to select only such exercises as are typical, and where several different methods exist for the measurement of the same quantity, only in rare instances has more than one been given. In a word, the book has been made as condensed as possible in order not to discourage the student with too many methods.

It has been thought advisable to include several exercises which are usually studied in physics, but these may be omitted if the student has already had sufficient practice with them.

For the convenience of the student there are appended tables of various physical constants which may be of service in the laboratory.

For the kind assistance given by friends the author would acknowledge his thanks, and especially to Prof. W. O. Atwater, who has so generously placed at his disposal the material for the section dealing with the determination of heats of combustion. To Messrs. P. Blakiston's Son & Co. I would express my thanks for permission to use several illustrations from Traube's "Physico-Chemical Methods."

If this book finds a place for itself in the hands of the student beginning the study of physical chemistry and proves to be of real service to him, it will have accomplished all that the author might wish.

FREDERICK H. GETMAN.

BALTIMORE, MD., April, 1904.

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LABORATORY EXERCISES

IN

PHYSICAL CHEMISTRY.

INTRODUCTORY.

MEASUREMENTS.

CHAPTER I.

WEIGHING.

WEIGHING, or the comparison of masses, is one of the fundamental and most common operations of the physico-chemical laboratory. For this reason great care should be exercised to secure a high-grade balance (Fig. 1) and set of weights (Fig. 2). Among the points to be given attention in the selection of a balance are the following:

1. When the beam is repeatedly stopped and again released it must invariably assume the same position.

2. When the beam is swinging the amplitude of the vibrations must diminish slowly.

3. Upon arrestment the pointer should stand directly over the middle division of the scale.

4. When the beam is released the points of support should act in unison.

These four conditions must hold equally well when the pans are loaded with the maximum weights for which the balance is designed.

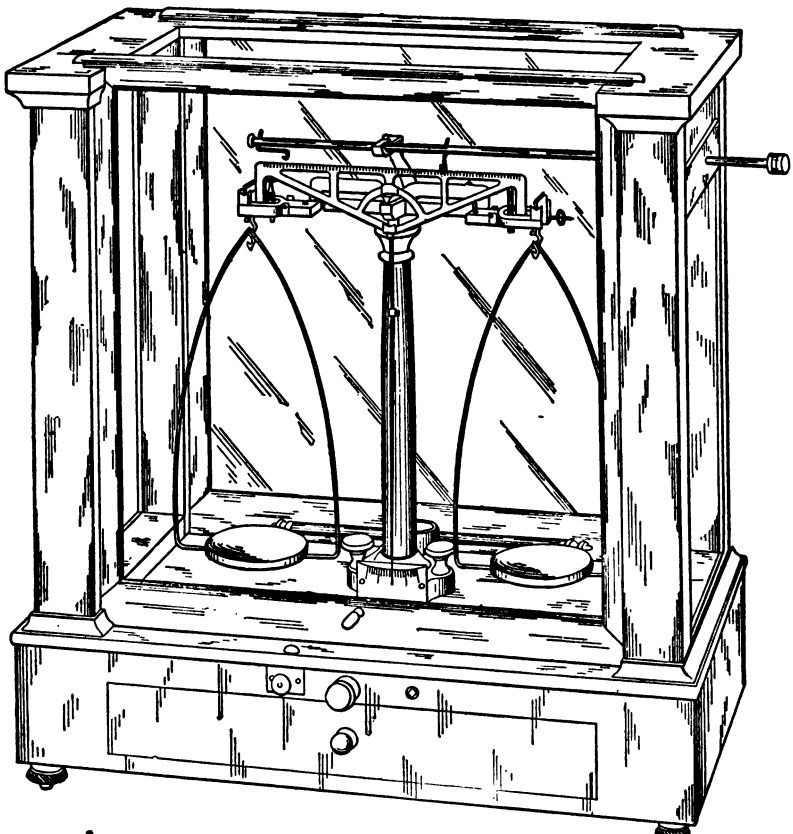


FIG. 1.

5. The arms should be of equal length.

6. The device for moving the rider must be provided with stops to prevent striking the beam.

7. The arrestment should work smoothly, and the doors to the balance-case must run freely.

8. The pointer must move close to the scale.

9. The divisions of the scale should be about one millimetre.

Care of the Balance.—The balance should stand on a firm table, or preferably on a stone slab resting upon masonry piers. It should not be exposed to the direct rays of the

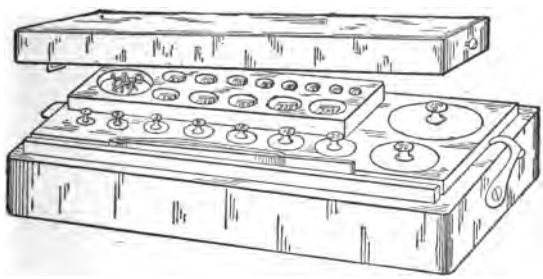


FIG. 2.

sun or to the direct radiation from any source of heat. Care must be taken as to the position of gas-flames, since a gas-flame a few feet from a delicate balance is sufficient to destroy the accuracy of the weighings. After the position of the balance has been determined it is levelled, and then should be disturbed as little as possible. To protect the instrument from rust and to exclude the influence of hygroscopic moisture during weighing, a small bottle of calcium chloride is frequently placed inside the balance-case. The knife-edges and the pans should occasionally be cleaned with a fine camel's-hair brush. Weights should be placed on the pans only when the balance is arrested, and likewise when weights or the object to be weighed are removed the beam should be stopped. Care should be taken to place the weights as nearly in the centre of the pan as possible, and

the pans should not be allowed to swing while making a weighing.

After weighing with heavy weights the zero-point must be redetermined. When making the final weighings the balance-case must be shut. Hot bodies must under no circumstances be introduced into the balance-case. All substances likely to injure the pans must be weighed in closed vessels.

The weights furnished with a high-grade balance are made of brass and platinum. The larger weights are of brass, either gilded or platinized, while the smaller weights are of platinum. Care should be taken to protect these weights from contact with mercury or any corrosive liquid. The weights should be handled only with the pincers, and should be returned to their places in the box immediately after using.

Weighing by Vibrations.—The first step in making a weighing by the method of vibrations consists in determining the zero-point, or the point at which the pointer comes to rest when the beam is unloaded. Since it would demand too much time to wait for the beam to come to rest, we determine the zero-point by observing the extreme positions of the pointer when swinging. Where only moderate accuracy is required it is sufficient to determine two successive turning-points and to take their arithmetical mean. If greater accuracy is desired, several turning-points are observed, taking care for the sake of reduction that an uneven number of observations is made. Five or seven are amply sufficient. We then take the arithmetical mean of the first, third, fifth, and seventh observations, and of the second, fourth, and sixth, and finally take the mean of these two means. This is the required zero-point.

Care should be taken to distinguish readings to the left

by a negative sign, or the middle point of the scale may be called 10 instead of 0, and thus negative signs avoided.

Having obtained the zero-point we place the body to be weighed on one of the scale-pans, and bring the beam nearly to the zero-point by means of weights placed on the other, and finally by moving the rider along the beam.

Now make another series of readings as above, then remove or add weights (one or more milligrams) according as the weights were too heavy or too light, until the position of equilibrium falls on the other side of the zero-point, and determine it by again observing the swings of the pointer. From these data we may calculate the weight of the body, W. Suppose the zero to have been a, and with the weight u let the new zero-point be denoted by b, while with the weight v let the corresponding zero-point be expressed by c. Then, since for small deflections the difference of the positions of equilibrium is proportional to the difference of the weights, we have

$$\frac{a-c}{b-c}=\frac{W-v}{u-v};$$

therefore

$$W=v+(u-v)\frac{a-c}{b-c}.$$

Due regard must be paid to the signs, for which reason it is simpler to number the scale-divisions as suggested above.

Illustration.—The value of the zero-point has been found to be 9.74.

Weight, mg.	Turning-point.				Mean.	Point of Rest.
3036	7.8		7.8	7.9	7.83	9.04
		10.3	10.2		10.25	
3037	9.5		9.4	9.3	9.40	9.95
		10.5	10.5		10.50	

Deviation for 1 mg. = 0.91 scale-division; hence, applying the formula, we have

$$W = 3036 + \frac{1 \times 0.7}{0.91} = 3036.77.$$

The amplitude of swing should amount to about three or four scale-divisions. Care should be taken to record the observations as given above.

Sensitiveness of a Balance.—The difference of indication for 1 mg. difference in weight is known as the *sensitiveness* of a balance.

This quantity is an important factor in determining the excellence of a balance, and a knowledge of it may be used to simplify the process of weighing.

The method of determining this quantity is at once apparent. The load for which the sensitiveness is sought is placed in each pan, and into one pan a small excess, so that the pointer is displaced about three divisions from the position of equilibrium.

This position is determined accurately by means of the method of oscillations; let us suppose it to be a. Now by adding w milligrams to the other pan the position of equilibrium is to be brought nearly as far on the other side of the centre and observed as before. Let this position be denoted by b. The sensitiveness is then $\frac{a-b}{w}$. This quantity should be determined for different loads at intervals of 10 grs., and the results plotted on coördinate-paper, loads as abscissæ and sensitiveness as ordinates.

The sensitiveness can be increased or diminished by means of a movable weight, which can be screwed up or down as desired. The time of vibration is a direct function of the sensitiveness, and should ordinarily be from 10 to 15

seconds. From the curve of sensitiveness we may gain assistance in weighing. Thus let us suppose that during a weighing the pointer is displaced 10 divisions from its position of equilibrium toward the right hand and let the load be 150 grams; then from the sensibility curve we learn that the sensitiveness corresponding to this load—that is, the displacement for 1 mg.—is 25. Therefore $\frac{10}{25}$ or 0.4 of a milligram is the amount which must be added to the weights in order that they may counterbalance the body.

Inequality of the Arms of the Balance.—This effect may be eliminated by two methods, known as those of Borda and of Gauss.

(*a*) *Method of Borda.*—The body to be weighed is counterbalanced by weights, shot, etc., and finally brought as near the position of equilibrium as possible by means of fine sand, bits of paper, or other suitable substances. The body is now removed and replaced by standard weights, until the balance is once more in equilibrium. The weight in the pan will now truly represent the weight of the body, since each has been placed under similar conditions. In using this method it is advisable to weigh by vibrations.

(*b*) *Method of Gauss.*—This method consists in weighing the body first in one pan and then in the other. Let us suppose that a body of which the true weight is W weighs A when placed in the right-hand pan and B when placed in the left-hand pan. If we denote by R and L the lengths of the right and left arms of the balance, then we have

$$WR = AL$$

and

$$WL = BR;$$

therefore

$$W^2 = AB,$$

or

$$W=\sqrt{AB}.$$

From this we learn that the true weight is the geometrical mean of the apparent weights.

Since we generally find A and B to be very nearly equal, no serious error is introduced by taking the arithmetical instead of the geometrical mean. Of the two methods, that of Gauss is to be preferred, since it consumes less time and gives more accurate results.

Reduction of Weighing to Vacuo. — For the *accurate* comparison of masses it is essential, when the weighing is made in air, that their densities be the same. For this reason, unless the body weighed has the same density as the standard weights employed, an error will be introduced. The reason is that if the body and the weights are of unequal volume, they will displace different amounts of air and hence lose weight unequally.

A correction for this may be easily deduced.

Let V, M, and Δ denote the volume, mass, and density of the body, while v, m, and δ have similar significations with respect to the weights. These quantities are so related that

$$V=\frac{M}{\Delta} \quad \text{and} \quad v=\frac{m}{\delta}.$$

Since every body loses in air the weight of the volume which it displaces, it follows that the body to be weighed loses λV and the weights λv, where λ is the density of the air. Since the weights after subtracting these losses are equal, we have

$$M-\lambda V=m-\lambda v,$$

or

$$M\left(1-\frac{\lambda}{\Delta}\right)=m\left(1-\frac{\lambda}{\delta}\right).$$

On account of the smallness of λ in comparison with Δ or δ, we may write

$$M = m\frac{1-\frac{\lambda}{\delta}}{1-\frac{\lambda}{\Delta}} = m\left(1+\frac{\lambda}{\Delta}-\frac{\lambda}{\delta}\right).$$

Illustration.—The correction of the apparent weight m of a quantity of water when weighed with brass weights ($\delta = 8.4$) amounts to

$$m \cdot 0.0012\left(\frac{1}{1}-\frac{1}{8.4}\right) = m \cdot 0.00106, \text{ or } 1.06 \text{ mg. for every gram.}$$

Calibration of a Set of Weights.*—In correcting a set of weights as many weighings must be performed as there are weights to be corrected. From these data a series of equations are formed from which the ratio of the arms of the balance and that of the weights to each other or to a convenient unit may be deduced.

With the set of weights used in analysis the following is the mode of procedure:

The larger weights are distinguished as

$$50', \quad 20', \quad 10', \quad 10'', \quad 5', \quad 2', \quad 1', \quad 1'', \quad 1'''.$$

A double weighing is performed with 50′ on one side and the rest of the weights on the other. Suppose it has been found that the balance is in equilibrium, i.e., the pointer is in the same position as when the balance is unloaded, when

Left.	Right.
50′	$20' + 10' + \ldots + r$ mg.
$20' + 10' + 10' + \ldots + l$ mg.	50′

* From Kohlrausch's Introduction to Physical Measurements.

Then the ratio of the arms of the balance is

$$\frac{R}{L}=1+\frac{l-r}{100{,}000},$$

and

$$50'=20'+10''+\ldots+\frac{r+l}{2}.$$

When $\frac{R}{L}$ has been determined a single weighing is sufficient for the other weights; for a weight p, on the right-hand pan, is, on account of the length of the arms, reduced to $p\cdot\frac{R}{L}$ when weighed on the left hand.

Example.—Let $r=-0.83$, $l=2.53$:

$$50'=20'+10'+10''+5'+1'+1''+1'''+0.85 \text{ mg.},$$

and

$$\frac{R}{L}=1.0000336.$$

Further, if it be found, when comparing $20'$ with $10'+10''$,

	Left.	Right.
that	$20'+0.91$ mg.	$10'+10''$

keeps the balance in equilibrium, in a balance with equal arms the equal weights would be

$$20'+0.91 \text{ and } (10'+10'')1.0000336,$$

or

$$10'+10''+0.67 \text{ mg.}$$

Suppose that from five weighings we have found

$$\begin{aligned} 50' &= 20'+10'+\ldots+A,\\ 20' &= 10'+10''\quad\quad +B,\\ 10'' &= 10'\quad\quad\quad\quad +C,\\ 5'+2'+1'+1''+1''' &= 10'+D, \end{aligned}$$

where of course A, B, C, D may be either positive or negative. From these equations the values of the five weights must be expressed in terms of some unit—the sum of the single grams being provisionally considered as one weight. If a comparison with a normal weight be not made at the same time, this unit is so chosen that the correction of the separate weights shall be as small as possible, which is the case when we consider the whole sum as correct—i.e., when we consider

$$50' + 20' + 10' + \ldots = 100{,}000 \text{ mg.}$$

Now it is easily found, by first of all expressing all the weights in terms of 10', that

$$50' + 20' + 10' + \ldots = 10 \cdot 10' + A + 2B + 4C + 2D = 100{,}000 \text{ mg.}$$

Calling, therefore,

$$\frac{A + 2B + 4C + 2D}{10} = S,$$

we have

$$\begin{aligned}
10' &= 10{,}000 \text{ mg.} - S, \\
10'' &= 10{,}000 \text{ ``} - S + C, \\
5' + 2' + \ldots &= 10{,}000 \text{ ``} - S + D, \\
20' &= 20{,}000 \text{ ``} - 2S + B + C, \\
50' &= 50{,}000 \text{ ``} - 5S + A + B + 2C + D, \\
&= 50{,}000 \text{ ``} - \tfrac{1}{2}A.
\end{aligned}$$

The proof of the correctness of the numerical work is easily found from the above to be that the sum of the corrections when expressed as numbers must be equal to 0 and the equations given above must be fulfilled.

Again, the following equations having been obtained by comparing the weights 5', 2', 1', 1'', 1''' with each other:

$$\begin{aligned}
5' &= 2' + 1' + 1'' + 1''' + a, \\
2' &= 1' + 1'' + b, \\
1'' &= 1' + c, \\
1''' &= 1' + d.
\end{aligned}$$

As in the previous case, calling

$$\frac{a+2b+4c+2d+S-D}{10}=s,$$

we have

$$\begin{aligned}
1' &= 1000\,\text{mg.} - s,\\
1'' &= 1000\ \text{“} - s+c,\\
1''' &= 1000\ \text{“} - s+d,\\
2' &= 2000\ \text{“} - 2s+b+c,\\
5' &= 5000\ \text{“} - 5s+a+b+2c+d.
\end{aligned}$$

In the same manner we proceed with the smaller weights, only remarking that usually the inequality of the arms of the balance no longer needs consideration.

In order to refer the table of errors to an accurate gram weight, it is necessary to compare the weights, or one of them, with a normal weight.

CHAPTER II.

VOLUME AND DENSITY.

Apparatus for Measuring Volumes.—The measurement of volumes is most satisfactorily accomplished by means of various forms of graduated vessels. The most important of these are:

(*a*) *Measuring-flasks* (Fig. 3).—These are made so as to contain, when filled to a certain mark and at a definite

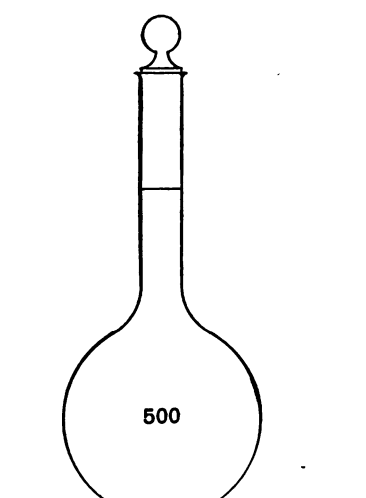


FIG. 3.

temperature, a definite volume. This volume, together with the temperature for which the flask is correct, is generally etched upon the glass. The chief sizes used in physico-

chemical work are 1000 c.c., 500 c.c., 250 c.c., 100 c.c., and 50 c.c. Occasionally flasks are marked with two lines, one for capacity and the other for delivery.

FIG. 4.

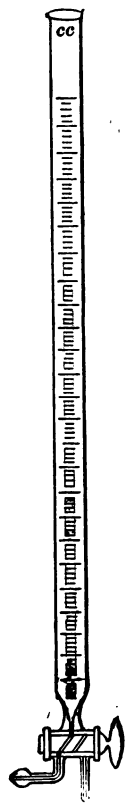


FIG. 5.

(*b*) *Pipettes.*—These are tubes open at both ends—the one opening being small, while the other is large enough to be covered by the finger (Fig. 4). The smaller sizes are made of straight tubing, while the larger ones have a bulb or cylinder in the centre. The chief sizes are 100 c.c., 50 c.c.,

25 c.c., 10 c.c., and 5 c.c. Pipettes of 50 c.c. capacity and graduated into cubic centimetres and tenths are extremely useful. Pipettes are filled by suction. When the liquid has reached the mark the larger end is covered by the finger and the liquid conveyed and delivered without loss.

(*c*) *Burettes.*—The form of burette best suited to the physico-chemical laboratory is that known as Mohr's burette. This consists of a graduated tube furnished with a

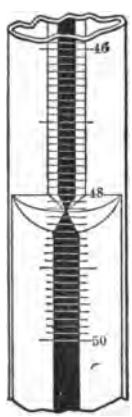


FIG. 6.

FIG. 7.

glass stop-cock at the lower end (Fig. 5). The most convenient size is a burette of 50 c.c. capacity divided into tenths. The best readings are obtained with burettes, which are furnished on the back with a blue enamel strip (Fig. 6) on a white ground. This device enables the observer to make a very sharp reading, which is little affected by parallax.

(*d*) *Eudiometers.*—These are graduated tubes closed at one end, and are used for the measurement of gases. They are graduated into cubic centimetres and tenths (Fig. 7).

The makers of apparatus for the measurement of volumes generally graduate it for use at either 15° C. or 17°.5 C., these temperatures being an average for laboratory temperatures.

Calibration of Measuring-flasks. — No measuring-vessel should be used until its accuracy has been tested. To verify the accuracy of a measuring-flask it is first cleaned and thoroughly dried and then weighed. It is then filled with water up to the mark, the inside of the neck being dried, and weighed again. The temperature of the water must be taken.

This weighing must now be corrected (1) for diminished density of the water due to excess of temperature over 4° C., and (2) for loss of weight in air.

Denote the apparent weight in air by W, and let λ be the density of the air. Assume the density of the brass weights to be 8.4. The volume of the water will be nearly W c.c., and it will lose in air $W\lambda$ grams, while the weights will lose $\frac{W\lambda}{8.4}$. The total loss will then be

$$W\left(\lambda-\frac{\lambda}{8.4}\right)=0.881W\lambda,$$

and the true we ght of water will be

$$W(1+0.881\lambda).$$

This exact weight will, however, occupy more than $W(1+0.881\lambda)$ c.c., for water at 15° C. has a greater volume than at 4° C. From the tables we learn that 1 c.c. of water at 4° C. occupies 1.000867 c.c. at 15° C. Therefore the actual number of cubic centimetres contained in the flask will be

$$W(1+0.881\lambda)1.000867.$$

Calibration of Burettes.—All graduated tubes, such as burettes, eudiometers, etc., would contain equal volumes in equal lengths if the bore of the tubes were uniform. Since this is rarely the case, the errors must be determined. A small calibration-gauge is attached to the lower end of the

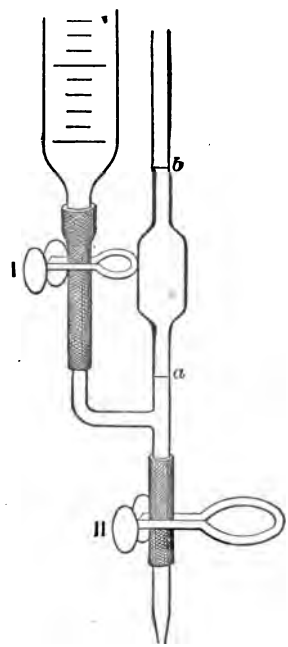


FIG. 8.

burette. This gauge (Fig. 8) consists of a small pipette holding 1 or 2 c.c. between the marks *a* and *b*, and a side tube below the mark *a*. When the apparatus is perfectly clean the burette and side tubes are filled with air-free distilled water and the level brought to the zero-division by means of the stop-cock on the burette. In the pipette the water is run out to the mark *a* by means of the spring-clip *II*.

Water is then run in through *I* from the burette until the level of the meniscus is at *b*. The reading of the burette is then noted. The water is next run out through *II* until the level is again at *a*, then run in through *I* up to *b*, the second reading on the burette being noted, and so on until the last division has been reached.

The readings of the burette then give directly the positions at which the contents reckoned from the zero-division are equal to 2, 4, 6, 8, 10, . . . c.c., and the correction at these places is the difference between the two values. These corrections should be written down on a sheet of heavy paper, which should be kept with the burette, or the results may be expressed by means of a curve. The intermediate values can be easily ascertained by interpolation. This same method of calibration may be applied to graduated pipettes.

Calibration of a Eudiometer.—The method of calibration here given is that due to the late Professor Bunsen. The eudiometer to be calibrated is fixed firmly in a vertical position over a wooden tray to catch any mercury which may be spilled. A small measuring-tube is provided to transfer the mercury to the eudiometer. This tube consists of a short piece of glass tubing closed at one end, the open end having ground edges. This tube should be provided with a wooden handle. The measuring-tube is filled with mercury, care being taken to avoid air-bubbles. When the measuring-tube is full it is closed by a ground-glass plate and the superfluous mercury is squeezed out.

This measure of mercury is then transferred to the eudiometer, pouring it down a funnel which should have a long glass tube attached to it by india-rubber tubing. The position of the top of the mercury meniscus is then read off by means of a reading-telescope.

Successive measures of mercury are added, care being taken always to read the meniscus after each addition and to avoid air-bubbles. Such a eudiometer is supposed to be read by means of a telescope, and to have mercury as the measuring fluid. From the data obtained in the calibration we can construct a table of relative capacities which is sufficient for most purposes. However, if it is desired to convert these into absolute values, the capacity of the measuring-tube must be found. To determine this the vessel should be filled and its contents weighed.

Calling W the weight of the mercury and t its temperature, the volume V of the tube in cubic centimetres will be,

$$V = \frac{W(1+0.0001815t)}{13.596},$$

where 13.596 is the density and 0.0001815 the coefficient of cubical expansion of mercury.

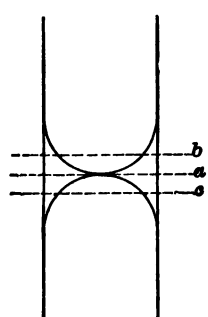


FIG. 9.

Before constructing a table it is well to notice that the mercury meniscus during calibration is turned the opposite way from the position it would occupy when in actual use. The space occupied by the gas will hence be greater than its calibration value by twice the space between the convex meniscus and its tangent plane (Fig. 9).

The value of this space can be determined as follows: First read the height of the meniscus in the usual manner, and then pour upon the surface of the mercury a few drops of mercuric chloride solution, when the surface will at once become horizontal. The height can now be read again, and the difference between the two readings will give the value of the space between the meniscus and the tangent plane. By doubling this we obtain the desired correction, which must be added to the calibration values in order to record the correct volume of the gas when the instrument is used in the inverted position.

Density (Specific Gravity).—The density of a body is the mass of unit volume.

For solids and liquids the mass of one cubic centimetre of water at 4° C. is taken as the unit of mass. From this we may then define the density of a body as the ratio of its mass to the mass of an equal volume of water at 4° C. The specific gravity of a body is the weight of unit volume. Since in a vacuum the ratio of the masses of bodies and the ratio of their weights are identical, both are expressed by the same numerical value. For gases, dry air is usually taken as the standard of reference. The vapor density of a gas is then the ratio of the mass of unit volume of the gas to the mass of an equal volume of dry air under similar conditions of temperature and pressure.

The reciprocal of the specific gravity is known as the *specific volume*, while the volumes occupied by the weights corresponding to the atomic and molecular weights are called the *atomic* and *molecular* volumes.

1. **Density of Solids.**—Of the many methods for determining the density of a solid the pyknometric method is the one most frequently employed in the physico-chemical laboratory. Numerous forms of this instrument have been

devised, but the simple form here shown (Fig. 10) is as satisfactory as any for determining the density of a solid. It consists of a glass bottle (having a capacity of 50 c.c.) provided with an accurately ground glass stopper. Through this stopper there passes a fine hole, through which the excess of liquid escapes when the stopper is inserted.

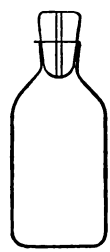


FIG. 10.

The use of the pyknometer involves three weighings: (1) pyknometer filled with air; (2) pyknometer filled with water; and (3) pyknometer filled with water and the substance of which the density is sought. Let the weight of the substance be denoted by w_s, the weight of water required to fill the pyknometer at temperature t by w_a, and the weight of the substance and water in pyknometer by w_b; then the specific gravity without corrections will be

$$s = \frac{w_s}{w_s + w_a - w_b}.$$

Reducing this to vacuum and to the temperature 4° C., we have

$$s = \frac{w_s}{w_s + w_a - w_b}(Q - \lambda) + \lambda,$$

where Q denotes the specific gravity of the water at temperature t and $\lambda = 0.0012$, the mean density of air in reference to water at 4° C.

If the temperature at the time of weighing the water is different from that at the time of weighing the water and substance, a correction must be introduced for the expansion of both water and glass. The above formula then takes the form

$$s = \frac{w_s(Q-\lambda)}{w_s + w_a - w_b + w_a[Q - Q_a + 3\beta(t-t_a)]} + \lambda,$$

where t and Q represent the temperature and specific gravity of water at the time of weighing the water and substance, t_a and Q_a the corresponding values at the time of weighing the water alone, and 3β the coefficient of cubical expansion of glass = 0.000025.

Should the substance of which the specific gravity is sought be soluble in water, other liquids may be used in its place, in which case the above formula must be multiplied by the specific gravity of the liquid substituted.

The method of procedure in determining the specific gravity of a solid with the pyknometer is as follows: The pyknometer is thoroughly cleaned, then dried with alcohol and ether, and then weighed. It is then filled with distilled water, care being taken to insure the absence of air-bubbles. The excess of water which exudes when the stopper is inserted is removed with filter-paper, and the pyknometer is weighed again. From these two weighings the weight of the water w_a is calculated. Finally the substance is weighed either inside or outside the pyknometer, and its weight gives us w_s.

By weighing the pyknometer containing the substance and filled with water we obtain w_b. From these data we may calculate the uncorrected specific gravity. To obtain the exact specific gravity it will be evident, from what has been said, that due regard must be paid to the temperature. Should it be required to determine the specific gravity of

substances which are too light, they may be made to sink by placing in a vessel of glass or in a wire cage, which remains in the pyknometer during all the weighings.

It is obvious that the pyknometer should not be grasped by the hands. The finer the state of aggregation of the solid the greater the error in the determination of its specific gravity. This is due largely to inclosed air or to adhering impurities.

2. Density of Liquids.—(*a*) *The Pyknometer.*—While the pyknometer just described may be used for the determination of the specific gravity of a liquid, yet another form, known as the Sprengel-Ostwald pyknometer (Fig. 11), is given

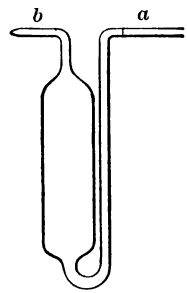


FIG. 11.

preference in most laboratories. With an instrument holding 25 c.c. determinations may be made with a probable error of about ± 0.00002.

The pyknometer is weighed (1) filled with air, (2) with water, and (3) with liquid of which the density is sought. The apparent weight of the liquid in air is denoted by w_s, and the weight of an equal volume of water by w_a. The uncorrected specific gravity is then $\frac{w_s}{w_a}$. Reduced to water at 4° C. and to vacuum, we have

$$s = \frac{w_s}{w_a}(Q - \lambda) + \lambda.$$

If the specific gravity of the liquid is determined at a temperature different from that at which the water is determined, the specific gravity is calculated from the following formula:

$$s = \frac{w_s}{w_a}[1 + 3\beta(t_a - t)](Q - \lambda) + \lambda,$$

where the additional symbols have the signification of the previous paragraph.

The usual size of the pyknometer is from 5 to 20 c.c. capacity, the larger sizes being selected for the most accurate determinations.

To carry out a determination of specific gravity with the Sprengel-Ostwald pyknometer, it is first cleaned, then dried with alcohol and ether, and then carefully weighed. It is then filled with the liquid under investigation either by means of the mouth or an aspirator, as shown in Fig. 12,

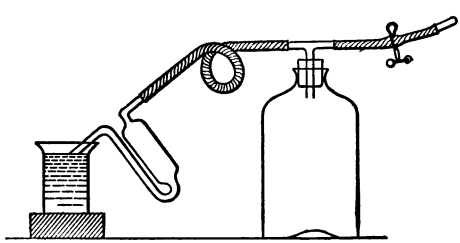


FIG. 12.

care being taken to avoid the introduction of air-bubbles. When completely filled the pyknometer is hung in a constant-temperature bath, so that only the upper tubes are out of water. If the determination is to be made accurate to the fourth decimal place, the temperature of the bath must remain constant to within 0.2°. The quantity of liquid in the pyknometer is regulated so that the smaller tube remains completely filled, while the liquid in the other

tube remains at the mark. This adjustment can be effected by the careful use of a bit of filter-paper and a glass rod with a drop of the liquid upon it. When the quantity of the liquid is properly adjusted the tubes are carefully wiped with filter-paper and a handkerchief and small glass caps put on. The whole apparatus is then dried, great care being taken that the heat of the hand does not reach the tubes. The pyknometer is then hung on the arm of the balance and weighed.

The same procedure is followed in weighing the pyknometer filled with water.

In this case, as in all density determinations, the water used should be air-free distilled water. For rapid determinations of the specific gravity of a liquid use may be made of a 1-c.c. pipette (Fig. 13) with tubes of almost capillary

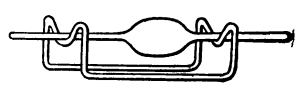


FIG. 13.

dimensions. It is filled by sucking the liquid up to a mark on the stem, and can be placed on the pan of the balance by means of a light, bent wire frame.

With this rough apparatus results accurate to the thousandths place of decimals may be obtained.

(*b*) *The Mohr-Westphal Balance.*—When it is desired to obtain only an approximation to the true density of a liquid this instrument is of great value, since the results can be secured in a very short time. The accompanying figure (Fig. 14) shows the instrument in its most common form. The beam *ABC* is pivoted at *B*, the longer arm *BC* having nine equally spaced notches at which riders may be placed. From the hook at *C* there hangs by a small platinum wire a float, *F*, while at the end *A* there is a

weight which serves as a counterbalance. The balance has been so adjusted that when the float hangs from the arm the beam should be in equilibrium, which is indicated by the points at *a* being opposite each other. If it is found that the points do not come opposite each other, the requisite adjustment may be made by means of the levelling-

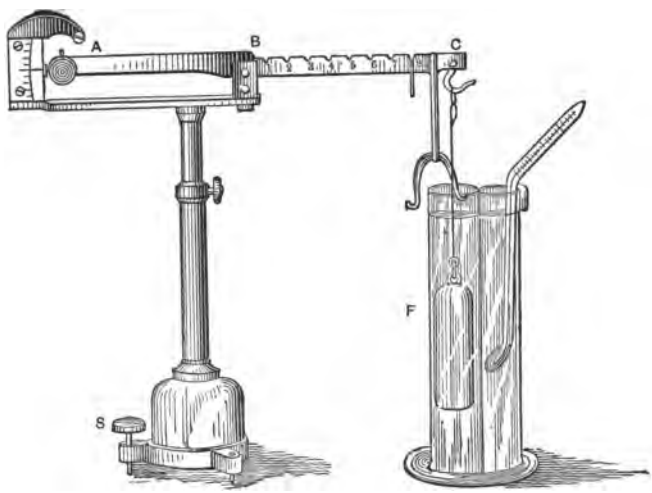


FIG. 14.

screw *s*. When the float is in water at 15° C., equilibrium is restored by placing one of the four riders (call it *A*) on the hook, this position being the tenth division of the arm. The remaining three riders are $B=A$, $C=\frac{A}{10}$, and $D=\frac{A}{100}$. If it is required to find the density of a liquid lighter than water, it is only necessary to place the liquid in the glass cylinder and allow the float to be immersed in it, and then to add riders to the beam until equilibrium is secured. Suppose *B* to be at 7, *C* at 4, and *D* at 8, then the density of the liquid is 0.748.

On the other hand, should the liquid be heavier than water, the rider A is first hung from the hook at the end of the beam. Let us suppose that the other riders have the following positions: B at 6, C at 2, and D at 6. Then the density of the liquid is 1.626.

The adjustments in air and in water must never be omitted. If the adjustment for water is not exact when A is hung from the hook, the final adjustment must be secured with the other riders and the corresponding correction applied to the results. This correction can be obtained by dividing the final reading by the weight on the beam; thus if the weight on the beam be 0.996 instead of 1, the final reading must be divided by 0.996.

Care must be taken to protect the knife-edges from rust, since the sensibility would be seriously impaired. By increasing the size of the divisions of the beam and taking greater care in the construction of the weights it is possible to obtain results of much greater accuracy. Kohlrausch and Hallwachs claim to be able to determine density to the sixth place of decimals by means of the hydrostatic principle.

3. Density of Gases (Vapor Density).—The determination of vapor density is one of the frequent operations of the physico-chemical laboratory.

The methods in use for the measurement of vapor density are:

(1) The method of Dumas.
(2) The method of Gay-Lussac.
(3) The method of Hofmann.
(4) The method of Victor Meyer.
(5) The method of Bunsen.

The general principles of all of these methods are well known to both the student of chemistry and the student of

physics. Perhaps the most simple, and certainly the most widely employed, is the method of Victor Meyer.

Method of Victor Meyer (Air Displacement). — A cylindrical glass vessel, *A* (Fig. 15), is furnished at the top with a longer tube, *a*. This vessel is placed in an outer glass tube, *B*, in which some substance is heated to boiling in order to maintain *A* at constant temperature. When substances of high boiling-points are used it is better to employ a vessel of copper for *B*. The tube *A* is closed with a rubber stopper, and by means of a side tube is connected with the eudiometer, *e*, which is filled with freshly boiled water. The air displaced by the vaporization of the substance in *A* is collected in *e* and its volume measured. The substance is weighed in a small thin-walled flask or weighing-tube, and is introduced into the tube *A* by means of the device shown in the illustration at *c*. The weighing-tube is placed upon the glass rod which is introduced into the side tube, and the entrance to the vaporizing vessel closed by means of an elastic-rubber tube which allows the glass rod to pass in or out freely. When the required temperature is reached the weighing-tube is dropped from the glass rod into the heated tube *A*, the bottom of which is cushioned with asbestos or glass wool.

Carrying out a Determination.—The vaporizing-tube is washed, dried with alcohol and ether, and the apparatus then assembled. A heating substance is chosen with a melting- or boiling-point 30–40° C. higher than the boiling-point of the substance under investigation. Among heating substances commonly in use may be mentioned: water, 100°; aniline, 183°; nitrobenzene, 211°; diphenylamine, 300°; paraffin, 350°; sulphur, 400°. When the apparatus is all set up the jacket is heated carefully, and as soon as air-bubbles cease rising in the liquid, which serves as the

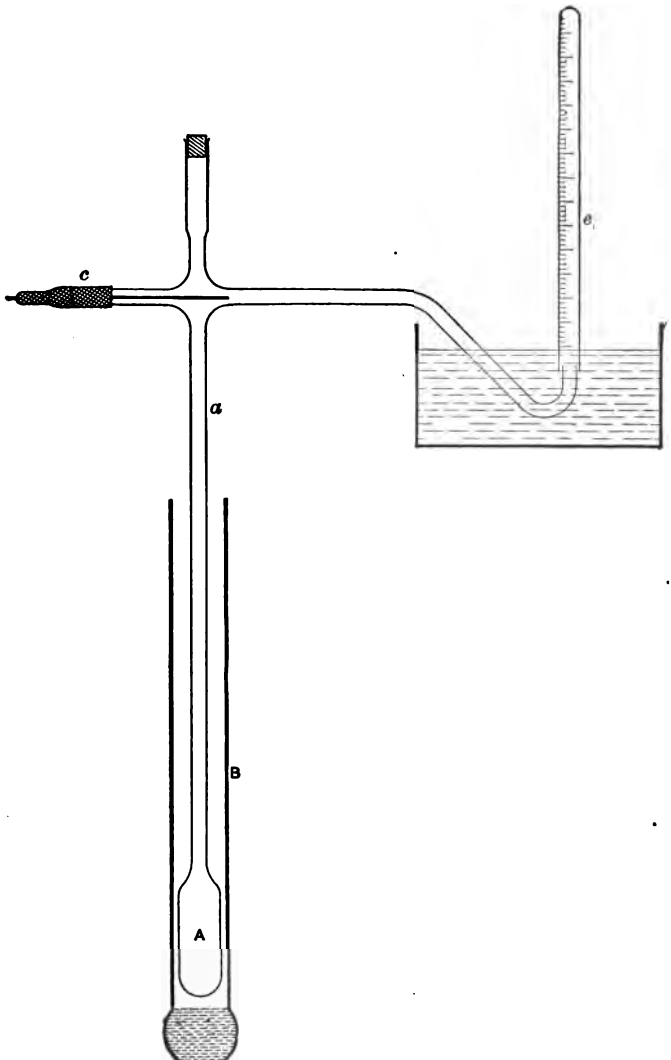


FIG. 15.

outlet to the vaporizing-tube, the weighing-tube is introduced and supported at *c*. After the temperature of the vapor-chamber has become constant and the measuring-cylinder *e*, filled with water, remains free from air for some time, the weighing-tube is dropped into *A* by pulling out the glass rod at *c*.

Immediately air-bubbles begin to rise in *e*, each molecule of displaced air corresponding to one molecule of the vaporizing substance. When no more air passes into *e* the connection with the vaporizing apparatus is broken and the volume of air is reduced to 0° C. and 760 mm. The volume of air should be at least 30–40 c.c. To produce this volume of air 0.1 to 0.2 gram of the substance is generally sufficient. Instead of using air as a medium the vaporizing-tube may be filled with hydrogen, nitrogen, or carbon dioxide.

The results of an experiment may be calculated from the data obtained, as follows:

Let g = weight of substance in grams;
v = volume of displaced air;
p = pressure in millimetres of mercury;
h = height of water column in measuring-cylinder;
f = vapor tension of water at $t°$;
t = temperature of enclosed air;
b = barometric pressure;
d = vapor density.

Then

$$d = \frac{g}{v_0 \times 0.001293} = \frac{g \times 760(1+0.00367t)}{vp \times 0.001293}.$$

The value of p is found from the expression

$$p = \left(b - \frac{h}{13.596}\right)(1 - 0.000181t) - f.$$

The value of f is to be found in the tables of vapor tension.

CHAPTER III.

VISCOSITY AND SURFACE TENSION.

VISCOSITY, or fluid friction, may be explained by the accompanying figure (Fig. 16). Let AB be a horizontal plate over which a liquid flows in the direction of the arrow. The layer of liquid in immediate contact with the surface remains at rest on account of adhesion, and the velocity of the different layers increases as the distance from the sur-

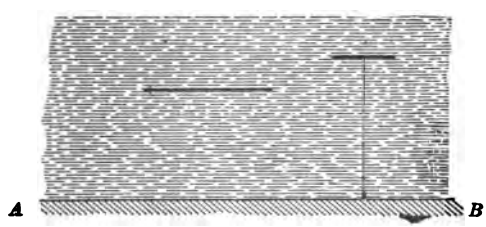


FIG. 16.

face increases. Thus we have a succession of layers of liquid each moving with a different velocity, the more slowly moving layer tending to retard the motion of the adjacent rapidly moving layer. Thus any horizontal layer is acted upon above by a tangential force in the direction of the motion of the liquid, and below by a second tangential force in the opposite direction. These two forces are what is known as viscosity, or fluid friction.

Flow of Fluid through a Long Tube.—Let l be the length of the tube and ρ its radius, p the pressure forcing the liquid through the tube, and v the velocity at a distance r from the

axis of the tube. Let us imagine a cylindrical portion of the fluid of radius r having the same axis as the tube. The surface of this cylindrical portion will move through the tube with a velocity v behaving like a solid rod. In like manner the cylindrical surface of radius $r+\Delta r$ will move through the tube with a velocity $v+\Delta v$ behaving like a hollow shell. Now the fluid layer between the "rod" and "shell" is subjected to just such conditions as any fluid layer between the plate and the surface of the liquid in Fig. 16. It has been found by experiment that the tangential force required to maintain a constant difference in velocity between two adjacent layers of liquid moving in parallel directions varies directly with the difference in velocity v and inversely with the distance x between the layers. That is,

$$F \propto \frac{v}{x},$$

or

$$F = \eta \cdot \frac{v}{x}; \quad \ldots\ldots\ldots \quad (1)$$

where η is a proportionality factor known as the *coefficient of viscosity*.

Equation (1) may now be written

$$F = \eta \frac{dv}{dr}, \quad \ldots\ldots\ldots \quad (2)$$

since Δv corresponds to v, and Δr to x.

This stress being tangential over the whole surface of the rod, the resistance becomes $2\pi rlF$, or $2\pi rl\eta \frac{dr}{dv}$. The force which overcomes this resistance is $\pi r^2 p$. The condition of equilibrium is then

$$\pi r^2 p = 2\pi rl\eta \frac{dv}{dr}, \quad \ldots\ldots\ldots \quad (3)$$

or

$$\frac{dv}{dr}=\frac{p}{2l\eta}r.$$

$$\int\frac{dv}{dr}=\frac{pr^2}{4l\eta}+K.$$

When $r=\rho$,

$$v=0 \quad \text{and} \quad K=-\frac{p\rho^2}{4l\eta}.$$

Therefore

$$v=\frac{pr^2}{4l\eta}-\frac{p\rho^2}{4l\eta}. \quad \ldots\ldots\ldots \quad (4)$$

From this we see that the velocity at each part of the tube is determined. To find the volume V of fluid which will flow through the tube in the time t, consider the cross-section

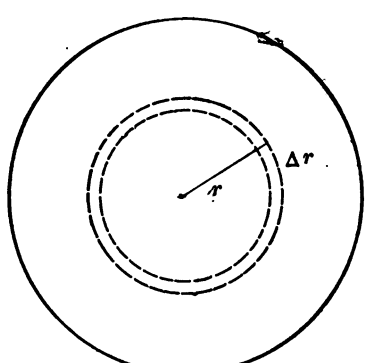


FIG. 17.

of the tube. The area of the section of radius $r+\Delta r$ (Fig. 17) is $\pi(r^2+2r\Delta r+\Delta r^2)$, and the area of the section of radius r is πr^2, from which we see that the area of the annulus is $2\pi r\Delta r$. The velocity over this annular area is v. So that the volume of liquid ΔV flowing across this area in time t is

$\Delta V = 2\pi r \Delta r \cdot v \cdot t$. Substituting in this expression the value of v in equation (4), we have

$$dV = \frac{\pi p t}{2 l \eta} r^3 dr - \frac{\pi p \rho^2 t}{2 l \eta} r dr,$$

$$V = \frac{\pi p t}{2 l \eta} \int_0^\rho r^3 dr - \frac{\pi p \rho^2 t}{2 l \eta} \int_0^\rho r dr,$$

or

$$V = \frac{\pi p \rho^4 t}{8 l \eta}. \quad \ldots \ldots \ldots \ldots \quad (5)$$

From this equation (5) it is possible to calculate the coefficient of viscosity η when the values of V, ρ, t, l, and p have been determined experimentally.

Solving equation (5) for η, we obtain

$$\eta = \frac{\pi p \rho^4 t}{8 V l}. \quad \ldots \ldots \ldots \quad (6)$$

The factor η may now be defined as the work necessary to move, in unit time, two layers of liquid surface in parallel but opposite directions; the distance moved being equal to the distance between the layers. If the liquid issues from the tube with a finite velocity, the coefficient must be diminished by $\frac{sV}{R\pi g}$, where g is the acceleration due to gravity, or 981, and s the specific gravity of the liquid. The constant R according to Hagenbach is 10.08, while Wilberforce and Finkener assign 8 as the more probable value. Since for the same apparatus all the factors entering into the expression for the coefficient of viscosity are constant with the exception of the specific gravity and the time, the corrected formula may be written

$$\eta = Kst - \frac{K_1 s}{t}.$$

The values of the constants K and K_1 are to be determined for each apparatus. The apparatus is so designed that the value of $\frac{K_1 s}{t}$ is extremely small in comparison with the value of η.

Frequently, instead of determining η, the *specific viscosity* is determined instead.

By the term specific viscosity is understood the time of outflow of the liquid at any one temperature divided by the time of outflow for water at 0° C. It is customary to introduce the arbitrary factor 100, so that the specific viscosity Q is determined by the expression

$$Q = \frac{100t}{t_w}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Measurement of the Coefficient of Viscosity.—(*a*) *Poiseuille-Ostwald.*—The method here given for the measurement of this quantity was originally devised by Poiseuille, and later improved by Ostwald. The apparatus required for the determination of the coefficient of viscosity is shown in Fig. 18.

The liquid is allowed to flow under its own pressure through the capillary *bd*. An accurately known quantity of the liquid is introduced at *f*, and by applying suction at *a* it is drawn up the tube until the liquid has risen above the mark *c*. The time occupied by the liquid in flowing down the tube from *c* to the lower mark, *d*, is carefully noted.

The capillary tube must be cleaned with the utmost care and then made thoroughly dry before beginning the experiment. Since the coefficient of viscosity changes on an average of two per cent. for each degree, care must be taken to insure constant temperature. This is insured by the simple arrangement shown in Fig. 19. The tube is fastened by

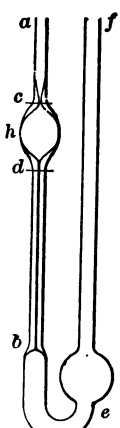


FIG. 18.

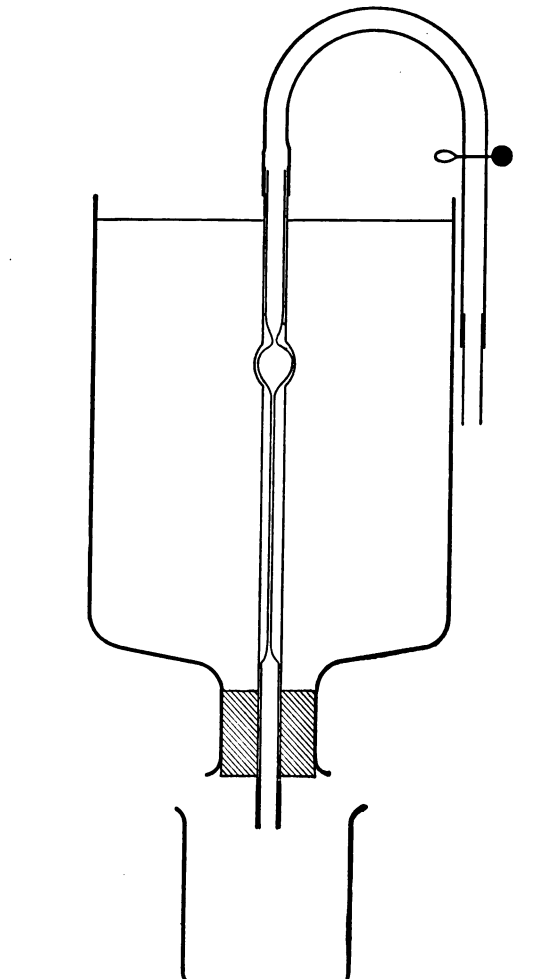


FIG. 19.

means of a rubber stopper in a large glass bell-jar holding about fifteen litres. This jar is filled with water and arranged so that the temperature may be determined accurately to within 0°.1 C. The apparatus is then filled with the liquid to be examined, due precautions being taken to exclude dust. By means of the rubber tube and pinch-cock shown in the figure it is possible to prevent the outflow of liquid until both the liquid and the water in the bath are at the same temperature.

When sufficient time has elapsed for equalization of temperature the pinch-cock is opened and the time required for the passage of the meniscus from the upper mark to the lower mark is measured by means of a stop-watch. The experiment should be repeated three or four times, and it is well to use several outflow-tubes. Before using the apparatus for the study of a liquid it should first be tested with water. The following table contains the constants of viscosity for water at different temperatures:

Temperature.	Poiseuille.	Sprung.	Traube.
0	0.018142	0.018136	0.01824
10	0.013351	0.013271	0.01333
20	0.010296	0.010214	0.01032
30	0.008212	0.008186	0.00819
40	0.006718	0.006725	0.00669

If the value of η in equation (6) is sought instead of the value of Q in equation (7), then it is necessary to determine accurately the value of ρ, V, l, and p. The values of ρ and V are accurately measured by means of mercury before the apparatus is assembled. The clean, dry tube is fastened to a millimetre scale and repeatedly filled as full as possible with clean mercury. The lengths of the mercury threads are measured, due care being taken to avoid parallax. If the length of a thread is l mm., and the gain in weight of the tube owing to the addition of the mercury is g mg., and

the temperature of the mercury is t, then the radius of the tube in millimetres is

$$\rho = \sqrt{\frac{g(1+0.000181t)}{13.596\pi l}}.$$

The value of the pressure p is calculated as follows: Let h_1 be the height of the lower mark above the opening of the capillary tube, and let h_2 be half the distance between the two marks; then $p = h_1 + h_2$. The following are the limits to the dimensions of the several parts of the apparatus which experience has shown give the best results:

$V = 4$ to 8 c.c.;
$\rho = 0.025$ to 0.030 cm.;
$l = 30$ to 40 cm.;
$h_2 = 1$ to 2 cm.

(*b*) *Method of Coulomb.*—Owing to the many experimental difficulties which beset the previous method and to its limitation to the less viscous liquids, the method of Coulomb is of considerable value in enabling us to determine relative or specific viscosities.

If a heavy disc suspended axially by a light vertical wire be immersed in a liquid and then set into torsional vibration, the ratio of any two successive oscillations in the same direction is a function of the viscosity of the liquid. If then the disc be set into vibration in one liquid and then in another, the ratio of the amplitude of successive swings in the same direction for each liquid will enable us to determine the specific viscosity. If η_1 be the coefficient of absolute viscosity of one liquid, r_1 the ratio of the amplitudes of any two successive oscillations in the same direction in this liquid, T_1 the period of oscillation of the disc, and γ_1 the damping constant, and η_2, r_2, T_2, and γ_2 represent the corresponding

quantities for the other liquid, then it can be shown mathematically that

$$\frac{\gamma_1}{\gamma_2}=\frac{T_2 \log r_1}{T_1 \log r_2}=\frac{\eta_1}{\eta_2}=Q.$$

The apparatus employed is shown in Fig. 20. It consists of a thin vertical wire attached by one end to a

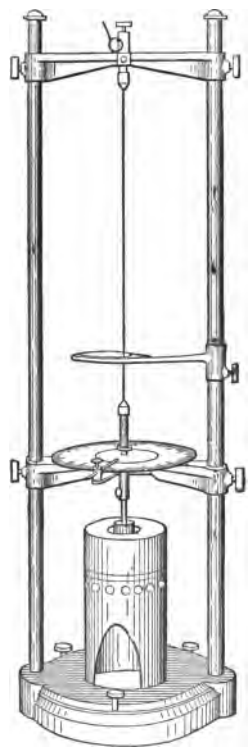


FIG. 20.

rigid frame, while the other end is attached by means of a heavy vertical rod to a divided circle and the disc which is to be immersed in the various liquids. The vessel in which

the liquids are placed is surrounded by an annular space in which some liquid can be placed to maintain an approximately constant temperature during a determination. After the liquid to be examined has attained the desired temperature the disc is twisted through an angle of about 180°. With a stop-watch the time of a dozen complete vibrations is taken. From this result the time T_1 of a single vibration can be calculated.

We now take a series of readings of the turning-points of successive vibrations to the right and to the left. The number of scale divisions through which the disc has turned in rotating from its extreme right position to its extreme left is the amplitude of the left vibration. Denoting these successive amplitudes to the right and to the left by L_1, L_2, L_3 . . . , and R_1, R_2, R_3 . . . , we have

$$\frac{L_1}{L_2}=\frac{L_2}{L_3}=\ldots=\frac{R_1}{R_2}=\frac{R_2}{R_3}=\ldots=r_1.$$

If these readings were taken upon the standard liquid of reference, then in a precisely similar manner the values of T_2 and r_2 can be found for a second substance which may be substituted in the equation previously given, and the value of the specific viscosity of the second substance determined. This method is of most value in working with oils or other extremely viscous liquids.

Surface Tension.—The effect of the unbalanced molecular forces within a liquid acting on the molecules near the surface is to exert a pressure on the interior of the liquid similar to that which would be produced by an elastic membrane. This pressure is due to the *surface tension* of the liquid.

If a capillary tube is dipped into a liquid which wets it,

the liquid rises within the tube to a height which is proportional to the surface tension.

Let Fig. 21 represent a capillary tube dipping into a vessel of liquid. The weight of the column of liquid in the tube is $\pi r^2 hdg$, where r is the radius of the tube, h the height

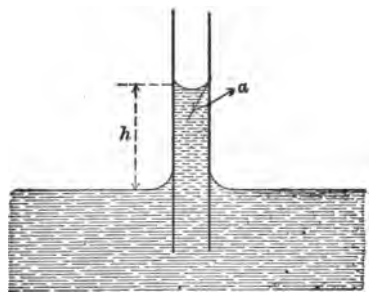


FIG. 21.

of the liquid, d its density, and g the acceleration due to gravity.

The force which balances this weight of liquid is the vertical component of the force due to the surface tension of the liquid surface at the walls of the tube. If γ be the surface tension and θ the angle of contact of the liquid with the wall of the tube, then this vertical component is $2\pi r\gamma \cos \theta$. Therefore

$$\pi r^2 hdg = 2\pi r\gamma \cos \theta,$$

or

$$h = \frac{2\gamma \cos \theta}{dgr} \quad \ldots\ldots\ldots \quad (1)$$

For water in glass tubes $\theta = 0$, so that (1) becomes

$$h = \frac{2\gamma}{dgr}, \quad \ldots\ldots\ldots \quad (2)$$

or

$$\gamma = \frac{hdgr}{2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Measurement of Surface Tension.—(*a*) *The Capillarimeter.*—The capillarimeter consists of a capillary tube of uniform bore 15 or 20 cm. in length and a millimetre scale of porcelain. The capillary tube has been ground flat upon one side, and upon this flat surface the millimetre scale is cemented. The tube extends 2 or 3 cm. beyond each end of the scale, and from the lower end of the scale extend two points which correspond to the zero-point. The adjustment of these points calls for considerable care.

The tube and scale are fastened by means of an arm and clamp to a rigid iron support furnished with a rack and pinion, which permits the tube to be raised and lowered (Fig. 22).

The tube is carefully cleaned, first with nitric acid, then with sodium hydroxide, and then with distilled water. After cleaning it is dried with 95% alcohol. No amount of care should be spared in cleaning the tube, since upon its cleanliness depends in large measure the success of the experiment.

The clean and dry tube is then clamped to the support, and by means of a plumb-line is brought into a vertical position. The liquid of which the surface tension is sought is placed under the tube in a small, clean glass vessel. By means of the adjusting-screw the tube is lowered until the two points just touch the surface of liquid in the dish. These points should touch the surface at the same time.

When the points are adjusted, then the liquid is carefully drawn into the tube, thus thoroughly wetting the walls. The best means of drawing the liquid into the tube is by means of a rubber tube fitted over the end of the

capillary, since by applying the mouth directly to the tube saliva is likely to get into the capillary. The liquid is drawn up several times to a height of 5 or 10 cm. above the posi-

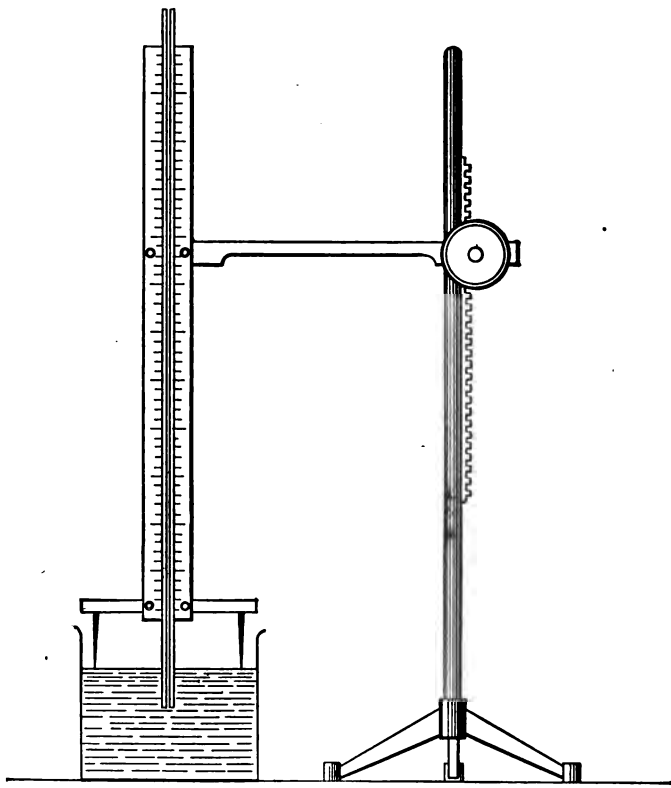


FIG. 22.

tion of equilibrium and then allowed to fall. The height of the lower edge of the meniscus is read five minutes after the last fall, care being taken to avoid parallax. The position of the meniscus will generally remain constant for several minutes, and then will fall slowly owing to imperfect

wetting of the tube. If a volatile liquid is being examined, the meniscus will rise. For exact measurements the observed height should be increased by one-third of the radius of the tube.

Care should be exercised to avoid air-bubbles or breaks in the column of liquid.

Measurements of the capillary rise are generally made at room temperature, and sufficient time should be allowed for the liquid and the tube to acquire the same temperature. For tubes of 0.15 to 0.20 mm. radius the temperature coefficient amounts to 0.1 to 0.2 mm. for 1° C.

Should the movement of the liquid be irregular and jerky, the presence of dirt in the tube is probably the cause. At the end of a series of determinations the tube should be rinsed out with distilled water and then closed with black gum-rubber caps.

The value of rh for water at 15° has been found to be 14.95.

CHAPTER IV.

SOLUBILITY.

By the term *solubility* we understand the extent to which one substance dissolves in another.

The study of solubility is of great importance in many physico-chemical investigations.

Though nine different classes of solutions may be distinguished, the one most frequently studied is the solution of a solid in a liquid. When a solid substance is dissolved by a liquid there is formed a homogeneous mixture which is inseparable by mechanical means. When the liquid has taken up, at a definite temperature, all the solid that it can the solution is said to be *saturated.*

In general there are two methods of obtaining saturated solutions.

(1) The finely powdered solid is brought into the liquid and agitated for some time at a definite temperature, until no more is dissolved.

(2 The solution is made as in (1), only at a higher temperature than that to which it is ultimately reduced.

In both of these methods, which give the same result if carefully executed, the same general rule holds that *in order for a solution to be saturated, it must always be in contact with the solid substance.* In making a saturated solution the suggestion put forth by Ostwald is valuable: "It is best to rub up a little of the substance with a few drops of the solvent, and then add so much of the magma to the almost

saturated solution that a cloudy liquid, which only clears up on long standing, is produced."

One of the most satisfactory arrangements for the determination of solubility has been devised by Noyes, a sketch of which is shown in Fig. 23.

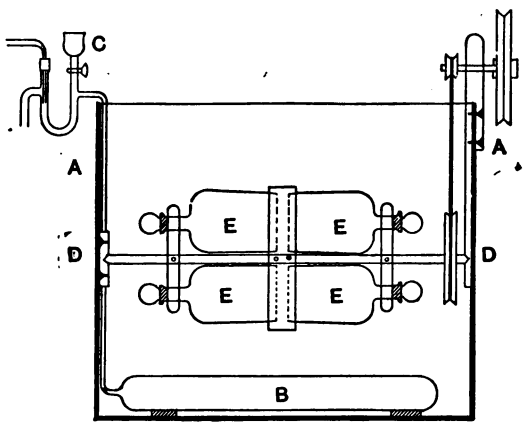


FIG. 23.

AA is a large water-bath on the bottom of which is placed an elongated glass bulb, *B*, the neck of which rises up by the wall of the bath and is bent over horizontally above. This is then connected with an Ostwald gas-regulator, *C*. The Ostwald gas-regulator (Fig. 24) consists of a U tube, the bend of which contains mercury, while the two arms are connected respectively with the bulb in the bath and with the gas-supply. The gas enters through *A*, which is inserted into one arm of the U tube and is moved down until it nearly touches the mercury. In the side of *A* there is a very small hole which prevents the flame under the bath being extinguished when the lower end of *A* is closed by the expansion of the liquid in *B*. When the bath cools the liquid in *B* (a 10% solution of $CaCl_2$) contracts,

the mercury in the regulator falls, and more gas is admitted to the burner. By proper adjustment it thus becomes possible to regulate the temperature of the bath automatically.

Upon the shaft *DD* are fastened the vessels containing the solutions together with some of the finely divided solid, and by means of a hot-air engine or other motor the shaft

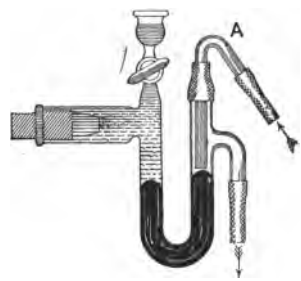


FIG. 24.

is made to revolve. In this way the vessels containing the solutions can be kept in continuous agitation.

Determination of Solubility. — The thermostat is adjusted for the desired temperature, the shaft *DD* being slowly revolved to insure complete uniformity of temperature throughout the liquid. The vessels *E* are filled with the solutions, care being taken to have present some of the solid. The vessels should be closed with rubber stoppers, since they are more water-tight than ground-glass stoppers. They are then fastened in the yokes on the shaft, and the motor started.

At temperatures above 40° C. less than an hour is sufficient to complete the saturation, provided the agitation is vigorous. For lower temperatures much longer times will be necessary.

When saturation is complete the motor is stopped, the

vessels are removed and their contents allowed to settle. Of course the vessels containing the solutions must be kept in the thermostat, otherwise some solid would either separate or pass into solution according as the room temperature was below or above that of the bath.

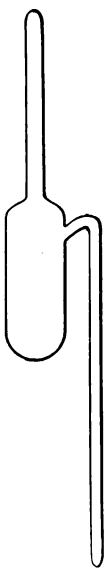


FIG. 25.

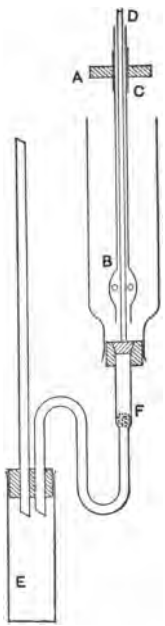


FIG. 26.

When the solutions have settled the quantity necessary for analysis is taken from the clear portion by means of a pipette. At high temperatures there is danger of loss due to evaporation of the solvent. The pipette shown in Fig. 25 is used for removing the liquid. The pipette is weighed before and after removing the liquid, the contents being washed out for analysis. The analysis may be effected either by evaporation and direct weighing of the dissolved

substance or by gravimetric or volumetric methods. The application of physical methods, such as the determination of the density or the electrical conductivity, may be of service in ascertaining the composition of the solution.

The expression of the results of the analysis may be either in terms of 100 parts of solvent or 100 parts of solution. The latter method, proposed by Etard, has the advantage that the curves representing solubility as a function of temperature are usually straighter, and great solubilities are more conveniently expressed since they cannot exceed 100. Substances which contain water of crystallization should be calculated in the anhydrous state.

Another form of solubility apparatus which has been used by Van't Hoff is shown in Fig. 26.

By means of a hot-air motor or a turbine the stirrer *AB* is driven. This stirrer is carried by means of the glass tube *C*; the rod *D* along the axis allows the liquid to flow out when saturation is attained through a plug of glass wool, *F*, into the weighing-tube *E*. The whole arrangement is obviously to be immersed in the thermostat.

CHAPTER V.

THERMOMETRY.

The Mercury Thermometer.—The instrument most frequently employed in the measurement of temperature is the mercury thermometer. To make a complete examination of this instrument both skill and time are necessary, but it is possible to-day, through the Physikalisch-Technische Reichsanstalt or through the United States Bureau of Standards, to obtain thermometers which have been tested most carefully in every respect. Thus it is assumed that every physico-chemical laboratory will have at least one corrected standard thermometer with which all other instruments may be compared.

It is only necessary then to give the method for the comparison of a thermometer with the laboratory standard.

Comparison of a Thermometer with a Standard Thermometer.—The two instruments are placed side by side in a good-sized vessel filled with some fluid. For temperatures below 100° C. water may be used, between 100° and 300° paraffin, while above this latter temperature a mixture of the nitrates of sodium and potassium is adapted to the purpose. The temperature of the bath must be raised very slowly (about 1° per minute), and provision must be made

for keeping the liquid thoroughly stirred. The readings should be taken by means of a reading-telescope, so that tenths of a division may be estimated. The correction for the exposed mercury thread is negligible, provided each thermometer projects out of the liquid by the same number of degrees. Furthermore, if each thermometer is made of the same kind of glass, no correction need be introduced for the difference in the expansion coefficients. At high temperatures the comparison may easily be inexact.

Calibration by Means of a Series of Fixed Temperatures.—Another method by which a thermometer may be examined between 0° and 100° involves the use of a series of transition temperatures.*

The following temperatures may be obtained at the melting-points of the corresponding hydrates:

$Na_2CrO_4 + 10H_2O$	19°.63 C.
$Na_2SO_4 + 10H_2O$	32 .379
$Na_2CO_3 + 10H_2O$	35 .2
$Na_2S_2O_3 + 5H_2O$	47 .9
$NaBr + 2H_2O$	50 .7
$MnCl_2 + 4H_2O$	57 .7
$Na_3PO_4 + 12H_2O$	73 .3
$Ba(OH)_2 + 8H_2O$	77 .9

Correction for Unheated Stem.—It frequently happens in using a thermometer that the whole stem of the instrument cannot be brought to the temperature to be measured. We must then calculate by how much the mercury thread would be lengthened were it all to be brought to the same temperature as the bulb.

* Richards, Zeit. phys. Chem., **26**, 690 and **28**, 313.

Let α = coefficient of expansion of the mercury = 0.000182;
β = " " " " " glass = 0.000024;
h = length of exposed column in degrees;
t_0 = mean temperature of exposed mercury column;
t = temperature indicated.

Then the correction, C, in degrees is

$$C = h(\alpha - \beta)(t - t_0).$$

If differences in temperature only are sought, this correction need not be applied.

The Fixed Points of the Thermometer.—From time to time it is well to test the so-called *fixed points* of a thermometer. This consists of two operations: (1) determination of the freezing-point; (2) determination of the boiling-point.

(1) *The Freezing-point.*—By means of a cork fasten the thermometer in a test-tube which is about half filled with distilled water, taking care that the bulb is completely immersed. The tube, which is provided with a wire stirrer, is sunk nearly to the neck in a mixture of ice and a little salt, the water being cooled about a degree below zero. The stirrer is operated slowly until ice begins to separate, when it is agitated vigorously. The mercury thread rises to the zero-point in about a minute, and remains there steadily. The difference between the reading and the indicated zero is the correction to be applied. The Beckmann freezing-point apparatus, to be described in a later chapter, serves admirably for the determination of the freezing-point.

(2) *The Boiling-point.*—The determination of the boiling-point is made with the apparatus shown in Fig. 27. The thermometer is placed in the steam-bath, so that the bulb and as much of the stem as possible are surrounded by steam, but care must be taken that the bulb is in the steam and not

in the water. After the thermometer has been in the steam for some time the position of the mercury thread is determined, and at the same time the reading of the barometer is taken. In reading the barometer the height of the column should be reduced to 0°, since the expansion

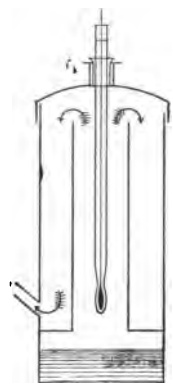


FIG. 27.

of the mercury often introduces an error of several millimetres.

The height of the barometer is given by the height of a column of mercury at 0°, which is maintained in equilibrium by gravity and the atmospheric pressure. The coefficient of expansion of mercury is 0.000182, so that if h be the height of the barometer as read at temperature t, its value h', reduced to 0°, is

$$h' = h - 0.000182 \cdot h \cdot t.$$

On account of the expansion of the scale the length of this also must be reduced to normal temperature. If β denotes the coefficient of linear expansion of the scale, the complete expression for the correction of the barometer reading becomes

$$h' = h - (0.000182 - \beta)ht.$$

Having obtained the corrected barometer reading, the temperature of the steam is found from the tables.

Without the tables the boiling-point may be determined to within 0°.1 for all pressures between 715 and 770 mm. by means of the formula

$$t = 100° + 0.0375(b - 760).$$

Illustration.—The reduced barometer reading is 742 mm. The mercury in the thermometer stands at 98°.8. The boiling-point according to the formula is $t = 100° - 0.0375 \cdot 18 = 99.33$. Therefore 100° is denoted by the division $98.8 + 0.67 = 99.47$, or the boiling-point as marked on the stem is too high by $100 - 99.47 = 0°.53$.

Expansion.—The coefficient of linear expansion is the change in length per unit of length of a body for a change of one degree in temperature.

The coefficient of cubical expansion is the change in volume per unit of volume of a substance for a change of one degree in temperature. It is shown in text-books of physics that the coefficient of cubical expansion is very nearly three times the coefficient of linear expansion. Since the coefficient of expansion usually increases with increase in temperature, we must distinguish between the true coefficient and the mean coefficient, which is determined on the assumption that the expansion is uniform for each interval of temperature.

The determination of the coefficient of cubical expansion of a liquid is of the most importance to the physical chemist.

Determination of the Coefficient of Cubical Expansion of Glass and Liquids.—Let d and d_1 denote the densities and v and v_1 the volumes of a liquid at the temperatures t and t_1, and let a represent the coefficient of cubical expansion. Then we have

$$v_1 = v\{1 + a(t_1 - t)\};$$

hence

$$a=\frac{v_1-v}{v(t_1-t)},$$

or

$$a=\frac{d-d_1}{d_1(t_1-t)}.$$

From this we see that the coefficient of cubical expansion may be calculated from two determinations of the density at two different temperatures.

The formula usually given for the calculation of the coefficient of cubical expansion is

$$a=\beta\frac{w}{w_1}+\frac{1}{t_1-t}\cdot\frac{w-w_1}{w_1},$$

where w and w_1 denote the weights of liquid contained in the pyknometer at the two temperatures t and t_1, and where β is the coefficient of cubical expansion of the glass. When β is known, then two weighings of the pyknometer at temperatures t and t_1 are sufficient for the determination of a. On the average β may be placed equal 0.000024.

If the value of β is sought, however, the pyknometer is filled with pure mercury and weighed at two temperatures, t and t_1. The coefficient of expansion of pure mercury may be taken as 0.000182. Then we have

$$\beta=0.000182\frac{w_1}{w}-\frac{1}{t_1-t}\cdot\frac{w-w_1}{w}.$$

The pyknometer is filled with mercury by dipping the point under the surface and alternately heating and cooling the pyknometer.

The apparatus used in determining the coefficient of cubical expansion of a liquid is shown in Fig. 28. The pyknometer (Fig. 28) is to be placed in a thermostat and heated to two different temperatures.

The pyknometer (Fig. 29) is to be heated in the vapor of boiling water and ether in the device shown in Fig. 30, the method being that due to R. Schiff.*

By means of an iron spoon the pyknometer is placed in a

FIG. 28.

FIG. 29.

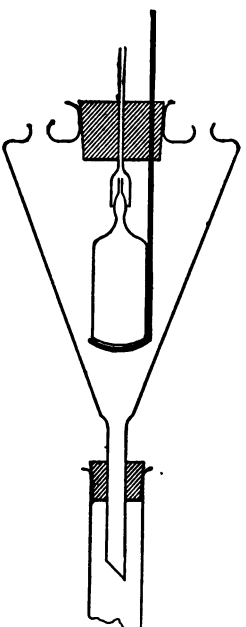


FIG. 30.

conical-shaped vessel, which is heated by the vapor of the liquid boiling in the vessel below.

The pyknometer is covered with a glass tube of the form shown, into which the liquid overflows from the pyknometer. The volume of the pyknometer at 34° is obtained from weighing the mercury which it contains after heating in the vapor of boiling ether. By weighing a second time

* R. Schiff, Berichte d. d. chem. Ges., 18, p. 1539, 1885.

after heating in the vapor of boiling water the coefficient of expansion β can be calculated.

The volume at 0° can be calculated approximately from the formula

$$v_0 = \frac{v_t}{1+\beta t}.$$

If the coefficient of expansion of the liquid is known, the coefficient of cubical expansion is calculated from the formula

$$a = \beta\frac{w}{w_1} + \frac{1}{t_1 - t}\cdot\frac{w - w_1}{w_1}.$$

The pyknometer when filled is heated in the vapors of appropriate liquids.

By determining the coefficients of expansion of a liquid at different intervals of temperature the relation between a and t is expressed by the formula

$$a = a + bt + ct^2,$$

where a, b, and c are constants determined by substituting the corresponding values for a and t.

Molecular Volumes of Liquids at their Boiling-points.—Closely allied to the determination of the coefficient of expansion of a liquid is the determination of molecular volume at the boiling-point. The method due to Ramsay and Lothar Meyer is the most convenient.

The pyknometer is weighed filled with air, then with distilled water at room temperature, and then at the temperature of boiling water.

Let w_t = weight of water at temperature t;

w_{t_1} = " " " " " t_1;

v_t, v_{t_1}, d_t, and d_{t_1} be the corresponding volumes and densities.

Then we have

$$v_t = \frac{w_t}{d_t} \quad \text{and} \quad v_{t_1} = \frac{w_{t_1}}{d_{t_1}}.$$

Hence

$$v_{t_1} - v_t = \frac{w_{t_1}}{d_{t_1}} - \frac{w_t}{d_t},$$

and

$$\beta = \frac{v_{t_1} - v_t}{t_1 - t} = \frac{\frac{w_{t_1}}{d_{t_1}} - \frac{w_t}{d_t}}{t_1 - t},$$

assuming $\beta = 0.000024$.

The volume for any boiling-point θ between t and t_1 is

$$v_\theta = v_t + \beta(\theta - t) = \frac{w_t}{d_t} + \beta(\theta - t).$$

Let θ = boiling of liquid of which molecular volume is desired;

d_θ = its density at $\theta°$;

w_θ = its weight at $\theta°$ = [(pyk. + liq.) − (pyk. + air)]; and

v_θ = volume of the pyknometer at temperature $\theta°$.

The molecular volume is then

$$v_m = \frac{m}{d_\theta},$$

where m is the molecular weight of the substance.

The pyknometer (Fig. 31) is made of Jena glass and holds about 2.5 c.c. The larger closed bulb is connected with a rather narrow capillary tube, the end of which is turned back upon itself.

The pyknometer is filled with the liquid under examination by means of the apparatus shown in Fig. 32.

A wide test-tube closed with a well-fitting rubber stopper is connected with an exhaust-pump and the outside air by means of a branched side tube provided with two stop-cocks. A calcium-chloride tube is inserted in the branch communi-

FIG. 31.

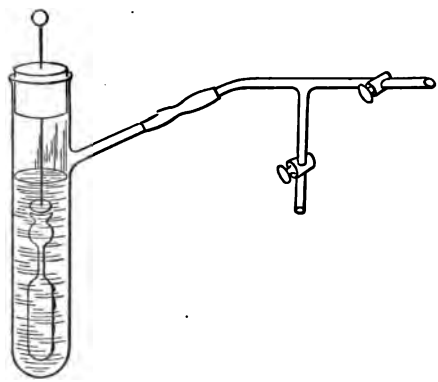


FIG. 32.

cating with the air. The bottom of the test-tube is filled with the liquid, and by means of a wire passing air-tight through the stopper the pyknometer is lowered until the point of the capillary is immersed. By alternately opening the stop-cocks to the pump and the outside air the pyknometer is filled with the exception of a very small air-bubble, which can be made to disappear upon subsequent heating.

If the liquid is heated at the same time that the air is alternately exhausted and readmitted, the time of filling is shortened.

The pyknometer is emptied by means of the same apparatus. It is suspended in an inverted position, and the two stop-cocks are alternately opened and closed. The pyknometer is dried by means of alcohol and ether.

When the vessel is filled it is hung in a boiling-vessel by means of a fine platinum wire which passes through the stopper. The boiling-vessel is provided with a reflux condenser, which if desired may be connected with a pressure-regulator.

For liquids which bump when boiling a capillary tube is passed through the cork and a current of air is gently drawn through the liquid.

The process in brief then is as follows: The pyknometer when filled with the liquid is suspended in the flask, so that the point of the capillary tube remains in the vapor. The liquid in the pyknometer expands and drops out of the tube, expelling with it the remaining air-bubble. When it has acquired the temperature of the surrounding vapor and no more liquid is expelled the boiling is stopped and the pyknometer allowed to cool. When the pyknometer has acquired the temperature of the room it is removed, carefully dried and then weighed.

CHAPTER VI.

MELTING- AND BOILING-POINTS.

Melting-point.—The determination of the melting-point is one of the commonest operations of the chemical laboratory, and yet the method usually employed is by no means accurate. The values obtained show variations of from 1° to 2°. These variations may be ascribed to the use of capillary tubes of too small diameter.

The most accurate method, however, cannot always be employed owing to scarcity of material, and hence the usual method of melting in a capillary tube attached to the stem of a thermometer must be resorted to. In the laboratory of the physical chemist, however, there is generally sufficient material at hand to permit of the employment of more accurate means.

A test-tube of about 3 cm. diameter is furnished with a carefully calibrated thermometer and a platinum stirrer, and in this is placed 15 to 20 grams of the substance. The test-tube is then placed in a large beaker containing some suitable liquid which can be heated several degrees above the melting-point of the substance. Water, oil, sulphuric acid, paraffin, concentrated solutions of sodium chloride, calcium chloride, etc., may be used. The liquid is heated several degrees above the melting-point of the substance, which has been roughly determined by the ordinary capillary-tube method.

As soon as the substance begins to melt it is stirred constantly. So long as any solid remains present the thermometer will remain stationary. This temperature is read and corrected for the exposed thread of mercury. By this method it is possible to attain an accuracy of 0°.1 C.

If more material is at the disposal of the experimenter, say 50 grams, it is possible to determine the solidifying point with great accuracy.

The beaker is replaced by a thermostat bath, which is maintained about 2° below the solidifying point of the substance. When the substance has been melted the test-tube is immersed in the thermostat bath and allowed to undercool. After sufficient time has elapsed to insure the undercooling of the substance a small particle of the solid is thrown into the molten substance. Solidification at once results and the thermometer rises to the true temperature of solidification.

There is perhaps no determination upon which the organic chemist places greater reliance than upon that of the melting-point of a compound, and yet the values obtained are by no means as accurate as at first sight appears. The student is specially referred on this point to Wiedemann and Ebert, Physikalisches Praktikum, 4th Edition, p. 159.

Boiling-point.—The boiling-point of a liquid is the temperature at which its vapor pressure and the external atmospheric pressure are in equilibrium.

Since the boiling-point is a function of the external pressure, it is customary to consider the temperature at which a liquid boils under 760 mm. pressure as the *normal* boiling-point.

The arrangement of Berthelot (Fig. 33) serves admirably for the determination of the boiling-point. The thermometer is placed in a long-necked flask the neck of which is sur-

rounded with a wide tube, as shown in the illustration. The liquid is placed in the flask, which has been carefully cleaned, and the calibrated thermometer inserted in the cork so far

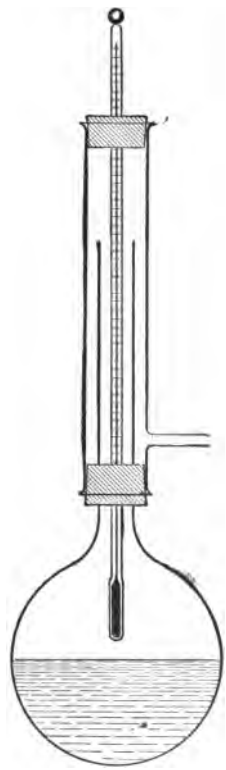


FIG 33.

that no correction need be applied for the unheated stem. The bulb under no circumstances should dip beneath the surface of the liquid. Correction must be made for the barometric pressure. Denoting the barometric pressure by b and the observed temperature by t, the normal boiling-point is nearly $t+0.0375(760-b)$. Should the boiling-point

be desired to the $\frac{1}{100}$ of a degree, the Jones apparatus (p. 72) should be employed.

For the determination of the boiling-point under varying pressures see Roloff, Zeit. phys. Chem., **11**, p. 25, 1893.

Depression of the Freezing-points of Solvents by Dissolved Substances.—In 1788 Blagden showed that the freezing-point of a solvent is depressed by the addition to it of any soluble substance.

Raoult found in 1887 that "if one molecule of any substance is dissolved in 100 molecules of any liquid of a different nature, the lowering of the freezing-point of this liquid is always nearly the same."

Let M = molecular weight of the dissolved substance;
g = number of grams of dissolved substance;
G = number of grams of solvent; and
Δ = the observed depression.

Then we have

$$M = \frac{C}{\Delta} \cdot \frac{g}{G},$$

where C is a constant for the solvent used. The value of C may be found experimentally by using as a dissolved substance a compound of which the molecular weight is known. The value of C may also be calculated by means of the equation

$$C = \frac{2T^2}{100L}.$$

For the derivation of this equation the student is referred to any good text-book of physical chemistry.

Apparatus a d Method.—The apparatus employed in determining the depression of the freezing-point is that designed by Beckmann, shown in Fig. 34. It consists of a stout test-tube, A, provided with a side tube, a thermome-

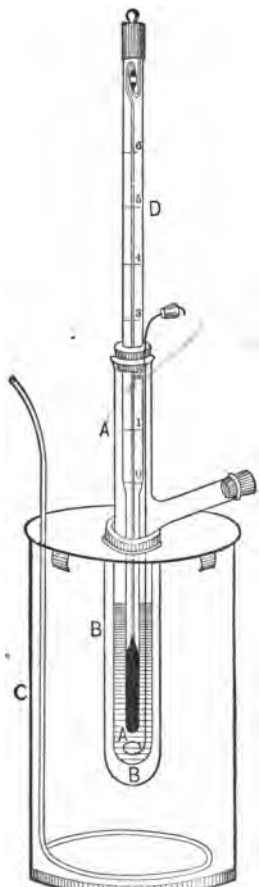


FIG. 34.

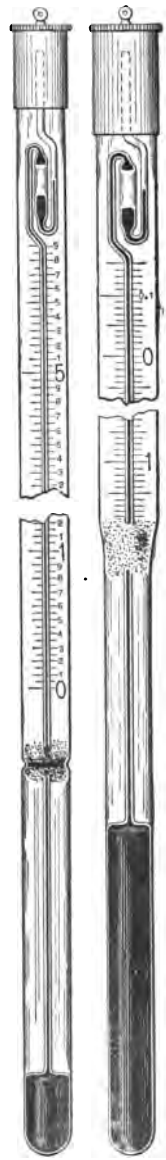


FIG. 35.

ter and stirrer. This stirrer consists of a ring of platinum-foil soldered to a thick platinum wire, or it may be made by bending a glass rod into a circle of sufficient diameter to allow the thermometer-bulb to pass through. By means of a cork this tube is fastened into a wider tube, *B*, which is supported in the large vessel *C* by means of a metallic cover. The vessel *C*, which is also furnished with a stirrer, contains the freezing-mixture. To prevent too rapid melting of the ice, *C* should be wrapped in felt or some other insulating material. The air-space between *B* and *A* serves to prevent too rapid or unequal cooling of the solution to be frozen. For accurate determinations the thermometer must be graduated to $\frac{1}{50}$ or $\frac{1}{100}$ of a degree.

The thermometer designed by Beckmann (Fig. 35) is best adapted to this work. Since the Beckmann thermometer is of special value in the physico-chemical laboratory, a brief description of it is given here.

This thermometer is a differential instrument—that is, it cannot be used for the determination of absolute temperatures, but only for the measurement of differences of temperature, such as the lowering of the freezing-point of water by a dissolved substance. In the accompanying illustration (Fig. 36) is shown the characteristic part of the thermometer.

By means of this reservoir at the upper end of the instrument the quantity of mercury in the thermometer-bulb can be increased or decreased, and thus the zero of the scale can be set at any arbitrary division. This adjustment of the amount of mercury in the bulb is accomplished by tapping or throwing the mercury either from the top or the bottom of the reservoir. With a little practice the experimenter soon acquires the necessary skill in "setting" his thermometer.

The total range of such a thermometer is usually 5° or 6°.

Each degree is divided into tenths and hundredths. Such thermometers can be used for both freezing-point and boiling-point determinations.

The first step in determining the depression of the freezing-point consists in the determination of the freezing-point of the pure solvent.

The inner tube, *A*, is accurately weighed and then sup-

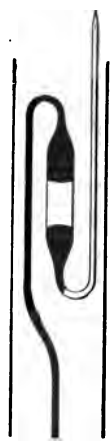


FIG. 36.

plied with 15 or 20 grams of the solvent, care being taken to keep the neck of the tube dry. After the introduction of the solvent the tube is again weighed accurately to centigrams. The tube is then placed in a vessel containing ice and salt or some other suitable freezing-mixture, and the solvent frozen. The tube is then removed from the freezing-mixture, and the solidified solvent is just melted by holding the tube in the hand and slowly operating the stirrer. When the solvent is melted the tube is placed in the air-jacket *B*, and with frequent stirring the solvent is again frozen. The

thermometer usually falls several tenths of a degree below the freezing-point, due to the undercooling of the liquid.

Freezing may be brought about by dropping into the liquid a minute crystal of the solid phase. As soon as crystallization begins the thermometer rises rapidly, and after thirty to sixty seconds attains a maximum, which is taken as the freezing-point of the solvent. Before reading the thermometer it should be gently tapped, with a pencil or with a cork on the end of a glass rod, to overcome the friction of the mercury thread in the capillary.

The degree of undercooling should never be allowed to exceed one degree, since otherwise errors are introduced. On the other hand, sufficient separation of ice will not occur unless 0°.5 undercooling takes place. For accurate work the apparatus should not be set up in a room the temperature of which differs more than a few degrees from the freezing-point of the solvent.

The temperature of the freezing-bath should not be more than 5 or 6 degrees below the freezing-point of the liquid under investigation.

When the freezing-point of the solvent is determined the solute is introduced into the tube *A*.

Solids are usually weighed in glass-stoppered weighing-tubes by means of which they are introduced into *A*.

Liquids may be introduced most conveniently by means of the capillary pipette shown in Fig. 37. The pipette is weighed before and after the introduction of the liquid.

The determination of the freezing-point of the solution then follows. It is carried out exactly as for the pure solvent.

After making a series of determinations of freezing-points of solutions the freezing-point of the pure solvent must be redetermined.

The freezing-mixture employed varies with the solvent or solution under investigation.

For water and aqueous solutions mixtures of snow and ice are most satisfactory; for benzene mixtures of ice and water are sufficient; for acetic acid the bath consists of water and a little ice; while for solvents, such as phenol and naphthalene, an ordinary thermostat is sufficient.

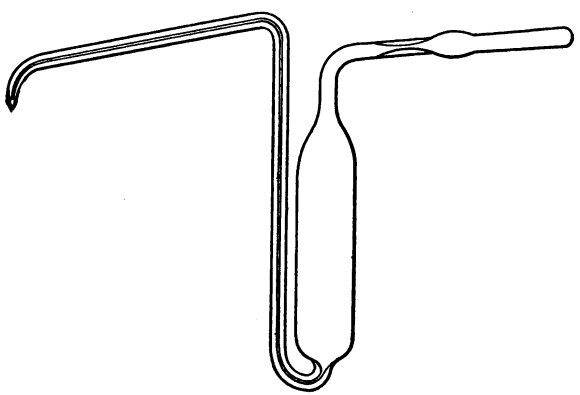


FIG. 37.

For hygroscopic solvents, such as acetic acid, special precautions must be taken to protect them from the moisture of the air.

The method as above outlined is essentially that given by Beckmann. It is sufficiently accurate for the determination of molecular weights, the molecular weight found being within 5% of the true value. For accurate determinations the method of Raoult must be employed, when with care the depression of the freezing-point may be determined to 0.001 of a degree.

The values of the constants for the more important solvents are here given:

Solvent.	Constant.
Water	18.5
Acetic acid	39.0
Benzene	50.0
Phenol	75.0
Naphthalene	70.0
Formic acid	27.7
Nitrobenzene	70.0
Ethlyene bromide	118.0

Dissociation by the Freezing-point Method.—As is well known, the molecular depression of the freezing-point of water produced by all non-electrolytes is a constant, 18.5. That is, all undissociated substances give a molecular depression of 18.5. All electrolytes, however, produce a molecular lowering of the freezing-point of water greater than 18.5. This increase in the molecular lowering is due to the dissociation of the dissolved substance.

The ratio of the observed molecular lowering to 18.5 is the coefficient i, introduced by Van't Hoff in the gas equation, expressing the relation between the number of molecules actually present in the solution to the number which would have been present had no dissociation occurred.

If n gram-molecules of a substance are weighed out and dissolved in water, if α is the percentage of n which is dissociated, and z is the number of parts into which a molecule of the substance breaks down, then we have in solution $n-n\alpha$ molecules and $zn\alpha$ parts of molecules. Therefore

$$i=\frac{n-n\alpha+zn\alpha}{n}=1+(z-1)\alpha,$$

or

$$\alpha=\frac{i-1}{z-1}.$$

This equation enables us to calculate the dissociation from freezing-point measurements.

Elevation of the Boiling-points of Solvents by Dissolved Substances.—It has long been known that the vapor pressure of a solution is lower than the vapor pressure of the pure solvent. Babo and Wüllner found that the lowering of the vapor tension is proportional to the amount of solute present; and for the same solution the depression for any temperature is the same fraction of the vapor tension of the pure solvent.

It was Raoult, however, who showed that *one gram-molecule of any substance dissolved in* 100 *gram-molecules of any solvent causes a constant relative depression of the vapor tension or elevation of the boiling-point.*

This relation is entirely analogous to the relation between the lowering of the freezing-point and the quantity of solute in a definite quantity of solvent. The value of the molecular weight of the solute in the given solvent is given by the formula

$$M = \frac{C}{\rho} \cdot \frac{g}{G},$$

where C is the constant for the solvent, ρ the observed rise in the boiling-point of the solvent, g the weight of solute, and G the weight of solvent.

Here, as in the freezing-point method, the value of C may be determined either experimentally or by means of the thermodynamic relation

$$C = \frac{2T^2}{100L},$$

where L denotes the latent heat of vaporization of the solvent.

Apparatus and Method.—Of the many forms of boiling-point apparatus which have been devised, perhaps the most convenient and accurate is that of Jones.

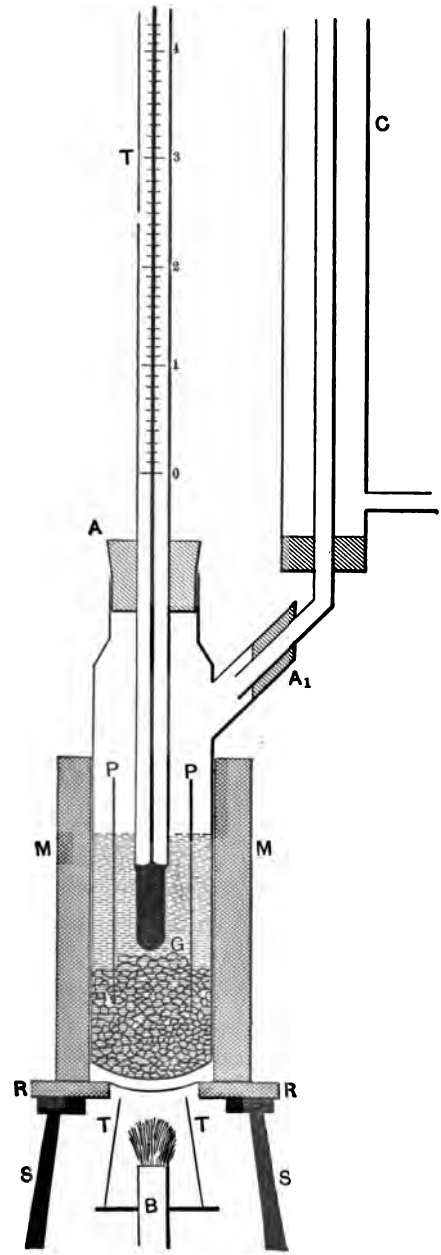
This apparatus is shown in Fig. 38.

Into the glass boiling-tube A are introduced some glass beads, while to the side tube A_1 the condenser C is attached. Into the beads a platinum cylinder, P, is inserted by placing the finger upon the top of the cylinder and gently shaking A. When the cylinder P is in place several bits of platinum-foil with the corners bent alternately in and out are dropped upon the beads at G. The liquid whose boiling-point is to be determined is introduced into A until the bulb of the thermometer is covered, as shown in the illustration. The liquid must not come within a centimetre and a half of the top of the platinum cylinder. The tube A is surrounded with an asbestos jacket, M, and rests on an asbestos board in which a circular hole is cut and over which is laid a sheet of wire gauze.

The tube A is heated by means of a Bunsen burner provided with a conical chimney. The flame used must be very small.

If the solvent is hygroscopic, it may be protected from moisture by closing the mouth of the condenser-tube with a calcium-chloride tube.

In making a determination of the boiling-point the first step is the adjustment of the thermometer, so that the top of the mercury thread comes to rest on the lower portion of the scale when the bulb is immersed in the boiling solvent. This is effected by pouring some solvent into the tube A, inserting the thermometer, and heating. When the solvent is boiling and as much mercury has been driven over into the reservoir of the thermometer as is possible, the thermometer is removed from the liquid, inverted for an instant,


T
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and then brought back to a normal position and given a tap sharp enough to cause the mercury to fall from the top to the bottom of the reservoir. The thermometer is then replaced in the apparatus, and the mercury thread allowed to become stationary. If the setting is as desired, the apparatus is ready for a determination; but if not, the above process is repeated until the mercury comes to rest within the first two degrees of the scale. Here, as with the adjustment of the thermometer for the freezing-point method, a little practice is necessary before the thermometer can be adjusted rapidly and satisfactorily. After the thermometer has been adjusted it is removed and the stem is carefully dried. The beads and platinum clippings are removed from *A*, and are carefully dried with alcohol and ether. The tube *A* and the platinum cylinder are also freed from adhering solvent. The glass beads are then poured into the tube, the platinum cylinder inserted and pressed down into the beads, and then the platinum clippings dropped into the platinum cylinder. The neck of the tube *A* is then closed with a ground-glass stopper, and the side tube closed with a cork. The whole is then placed in a beaker and weighed to centigrams. The solvent is then introduced, and the apparatus is weighed again. After the solvent is weighed the apparatus is assembled as shown in the illustration, and the boiling-point of the pure solvent determined. The size of the flame must be very carefully regulated, so that the boiling is vigorous but not violent. This is best attained by means of a screw pinch-cock on the gas tubing. Some time is necessary for the establishment of the equilibrium temperature between the pure solvent and its vapor. When the mercury column is stationary the thermometer is tapped gently with a pencil or special hammer and the reading taken. Great care should be taken to read the thermometer only when the

mercury thread is rising. Indeed this is a general rule of thermometry. When the boiling-point of the pure solvent has been established a tube containing the solute pressed into pellets is weighed, and a suitable number of these poured into the solvent. Of course the solvent should be allowed to cool before removing the stopper for the introduction of the solute, otherwise the solvent will escape as vapor. The weighing-tube is then reweighed, and the amount of substance introduced thus ascertained. The boiling-point of the solution is determined in exactly the same way as the boiling-point of the pure solvent. It usually takes less time for the attainment of equilibrium with a solution than with the pure solvent.

It is obvious that in all boiling-point determinations the barometer must be carefully observed.

If the determination of the boiling-point of the solution is made quickly after the boiling-point of the solvent has been ascertained, no correction is necessary for change in pressure, since it will be so small. In making a series of determinations it will be found convenient to set up two pieces of apparatus, in one of which the pure solvent is kept constantly boiling. In this way we are made independent of changes in atmospheric pressure. A small correction should be introduced for the evaporation and condensation in the condenser. According to Beckmann the amount of liquid suspended in the boiling-tube is, for very mobile liquids, from 0.15 to 0.2 gm., while for water it is about 0.35 gm.

The following table gives the values of the boiling-point and the boiling-point constant for the most common solvents:

Solvent.	Boiling-point.	Constant.
Ethyl ether	34°.97	21.6
Carbon disulphide	46 .2	23.5
Acetone	56 .3	17.2
Chloroform	61 .2	35.9
Ethyl acetate	74 .6	26.8
Ethyl alcohol	78 .3	11.7
Benzene	80 .3	26.1
Water	100 .0	5.1
Acetic acid	118 .1	25.3
Ethylene bromide	131 .6	64.5
Phenol	132 .3	30.4
Anilin	182	32.2

CHAPTER VII.

CALORIMETRY.

Quantity of Heat.—In order to measure the quantity of heat which is lost or gained by a body when its temperature changes or when its physical state changes, the unit commonly employed is that quantity of heat which acting on a given mass of water alters its temperature by a definite amount. Since the specific heat of water is not the same for all temperatures, it is necessary to specify between what two temperatures the water is to be taken. The following units are all in use:

(1) The heat required to raise 1 gram of water from 0° C. to 1° C.

(2) The heat required to raise 1 gram of water from 3°.5 C. to 4°.5 C.

(3) The heat required to raise 1 gram of water from 14°.5 C. to 15°.5 C.

(4) The heat required to raise 1 gram of water from 18°.0 C. to 19°.0 C.

(5) The heat required to raise 1 gram of water from 0° C. to 100° C.

Each of these units is called a *calorie.*

It is obviously necessary to specify what calorie is used. In thermochemical measurements it is customary to employ the calorie defined in (5). This is known as the *large calorie.* For measurements at room temperature the calorie defined

in (4) is employed. For methods involving melting ice (Bunsen's ice-calorimeter, etc.) the *mean calorie* is used. This is the one-hundredth part of the heat necessary to raise 1 gram of water from 0° C. to 100° C. The mean calorie and the calorie at 18° do not differ more than one per cent. at most. The proposition has been made to adopt as the unit of quantity of heat 4.2×10^7 ergs, and to call this unit the *joule*, thus expressing heat values in terms of their equivalent energies.

Specific Heat.—By the specific heat of a body we understand the number of calories necessary to raise 1 gram of the substance 1° C. Since the specific heat is found to vary with the temperature, the temperature at which a determination of the specific heat is made should always be specified.

Determination of the Specific Heat of Solids. — The method most usually employed is known as the *method of mixtures*, and consists in heating a given mass of the solid to a definite temperature, and then immersing it in a known mass of water, the initial and final temperatures of which are observed. The vessel containing the known mass of water is called a *calorimeter*.

Let W = weight in grams of solid of which the specific heat is to be measured;
T = temperature to which the solid is raised;
C = specific heat of the solid;
w = weight of water in calorimeter;
t = initial temperature of water in calorimeter;
θ = final temperature of water in calorimeter.

Then we have

$$CW(T-\theta) = w(\theta - t),$$

or

$$C = \frac{w(\theta - t)}{W(T-\theta)}. \quad \ldots\ldots\ (1)$$

The calorimeter, the stirrer, and the thermometer, however, take up a portion of the heat lost by the solid, and consequently equation (1) must be corrected.

If the mass of the calorimeter be M, and the specific heat of the material of which it is made be S, then MS is its so-called *water equivalent.*

In the same manner the water equivalents of the thermometer and stirrer may be found by multiplying their respective masses m and m' by their specific heats s and s'. Equation (1) then becomes

$$C = \frac{(w + MS + ms + m's')(\theta - t)}{W(T - \theta)}. \quad . \quad . \quad . \quad (2)$$

Heating-vessel.—If it is not desired to heat the substance higher than 100°, the form of apparatus shown in Fig. 39 is

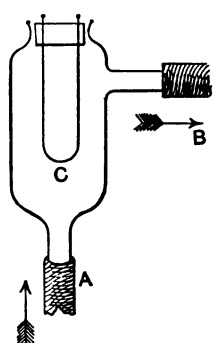

FIG. 39.

very convenient. The steam is passed in and out by means of the india-rubber tubes A and B, and thus the solid which is placed in C is heated to 100°. This inner tube is closed during the heating by a stopper carrying the thermometer. A short-necked retort of copper in which nitrobenzene, diphenylamine, etc., may be kept boiling is frequently of

value. A stopper placed in the neck of this retort carries a test-tube in which the substance to be heated is placed, and also an exit-tube for the vapor of the heating agent. The heating device should be as far away from the calorimeter as possible, and if it is necessary to have it close at hand the calorimeter must be screened by means of asbestos board.

The substance, especially if it be a poor conductor of heat, is used in small pieces. It is weighed in a weighing-tube, and after introducing it into the heater the tube is reweighed and thus the weight of substance used ascertained.

The Calorimeter.—The calorimeter consists of a thin-walled cylindrical metallic vessel of at least 500 c.c. capacity. It is preferable to have the calorimeter made of platinum on account of its permanence and small heat capacity, but the expense frequently prohibits its employment. Perhaps the best substitute is nickel, which may be used with water and neutral or alkaline solutions. A calorimeter made of silver and gold-plated on the inside is also a good substitute for one of platinum.

To prevent loss of heat to surrounding bodies the calorimeter is placed in a slightly larger polished brass vessel of cylindrical section. The calorimeter rests upon three pieces of cork, which serve to insulate it from the bottom of the containing vessel.

This brass vessel in turn is placed coaxially inside a larger double-walled brass vessel. The space between the walls is filled with water, and the annular space between the double-walled vessel and the polished brass vessel is about 5 cm.

The calorimeter is provided with a cover, which should be made of some poor conductor. The stirrer is one of the

most important parts of the calorimeter, since it is essential that all parts of the liquid shall be at the same temperature. Many forms of stirrer have been devised, but as efficient as any is that described by Ostwald. It consists of a circular plate nearly filling the section of the calorimeter. In this plate are cut the necessary holes for the thermometer and any other pieces of apparatus which may be in the interior.

The plate has H-shaped openings cut in it, the two

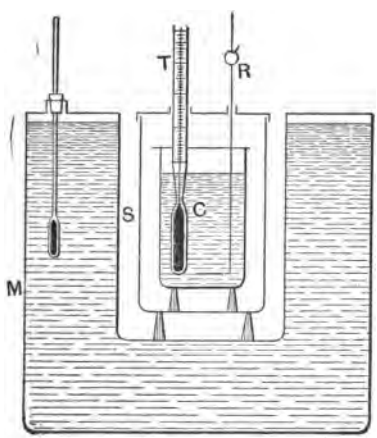

FIG. 40.

flanges being bent out of the plane of the plate in opposite directions. By means of the flanges the stirrer as it is moved up and down gives to the contents of the calorimeter a whirling motion, thus effecting a very complete mixing.

If a number of calorimetric measurements are to be made, the stirrer may be operated mechanically.

A cross-section of a calorimeter is shown in Fig. 40. The thermometer employed is usually a Beckmann instrument graduated to $\frac{1}{100}$ of a degree. The specific heats of the metals most frequently used in the construction of calorimeters are here given:

Platinum	0.032
Silver	0.057
Nickel	0.110
Brass	0.094

Under no circumstances should glass be used in the construction of a calorimeter.

Method of Operation.—The substance of which the specific heat is to be determined is placed in the heater and allowed to acquire the temperature of the vapor of the boiling water. The initial temperature of the liquid in the calorimeter is carefully noted. When the substance has acquired the desired temperature it is transferred to the calorimeter, precautions being taken to avoid loss of heat by radiation.

The liquid in the calorimeter is stirred constantly, care being taken that none of the substance is removed by the stirrer from the liquid.

The thermometer is read as directed below, and the final reading taken. The process is theoretically a simple one, but practically it is fraught with difficulties. These difficulties are: (1) loss of heat by radiation; (2) loss of heat to the calorimeter; (3) loss of heat to the stirrer; and (4) loss of heat to the thermometer. The corrections to be applied for each of these losses will be considered in the order given.

(1) **Loss of Heat by Radiation.**—Rumford proposed to correct for this loss by making a preliminary experiment to determine approximately the rise in temperature of the calorimeter and then in the final determination to cool the calorimeter before the introduction of the heated substance to a temperature below that of the surrounding air by an amount equal to one-half of the rise. In this way the calorimeter would receive heat during the first half of the experiment and give out heat during the second half. Since the temperature rises most rapidly at the beginning, this method

of correction is far from satisfactory and for all accurate work the method of Regnault is employed.

(1) *First Period.*—Before the investigation is commenced the temperature of the calorimeter is noted every minute for ten minutes. Assume these temperatures to be $t_0, t_1, t_3, \ldots t_{10}$. If the experiment begins when t_{10} is noted, t_{10} cannot be determined directly, but it is found thus:

$$t_{10} = t_9 + \frac{t_0 - t_9}{9}.$$

That is to say, t_{10} is equal to t_9 plus the average rate of change of temperature during nine minutes.

(2) *Second Period.*—The beginning of this period is simultaneous with the commencement of the experiment. At first a rise in temperature is noted, then a maximum is reached, after which the temperature falls. This period is assumed to continue for ten minutes, since after that interval of time the decrements of temperature are equal.

For this period we have $t_{10} = \tau_0$ at the beginning, and $\tau_1, \tau_2, \tau_3, \ldots \tau_{10}$, the temperatures noted each minute during the period.

(3) *Third Period.*—During this period the change in temperature due to radiation is uniform. The temperatures observed at intervals of one minute are $\tau_{10} = \theta_0$ and $\theta_1, \theta_2, \theta_3, \ldots \theta_{10}$.

Let the temperature changes during the first, second, and third periods be denoted by Δ^t, Δ^τ, and Δ^θ.

The average temperature changes for the first and third periods correspond to the average temperatures t_5 and θ_5 of these periods, or

$$\Delta_5^t = \frac{t_0 - t_{10}}{10} \quad \text{and} \quad \Delta_5^\theta = \frac{\theta_0 - \theta_{10}}{10}.$$

Now it may be assumed that the differences in the temperature changes are proportional to the differences in the

corresponding temperatures. Let τ_n and Δ_n denote any given values for the second period, then we have

$$\frac{\Delta_n^\tau - \Delta_5^t}{\Delta_5^\theta - \Delta_5^t} = \frac{\tau_n - t_5}{\theta_5 - t_5},$$

or

$$\Delta_n^\tau = (\tau_n - t_5)\frac{\Delta_5 - \Delta_5^t}{\theta_5 - t_5} + \Delta_5^t.$$

If we substitute for τ_n the average of the temperature noted at the beginning and the end of the nth minute, and for n all the values of n from $n=0$ to $n=10$, the loss of heat due to radiation for each of the ten minutes of the second period is obtained. If now to the final temperature τ_{10} we add the sum of these differences, we obtain $\tau_{10}+\Sigma\Delta$ as the corrected final temperature.

The calculation is performed thus:

$$\Sigma\Delta = (\Delta_1^\tau + \Delta_2^\tau + \Delta_3^\tau + \ldots \Delta_{10}^\tau)$$
$$= \left(\tau_1 + \tau_2 + \tau_3 + \ldots \tau_9 + \frac{\tau_0 + \tau_{10}}{2} - 10t_5\right)\frac{\Delta_5^\theta - \Delta_5^t}{\theta_5 - t_5} + 10\Delta_5^t.$$

The method of correction is best illustrated by an example:*

Room temperature = 23°.5.

Time.	Temp.	Time.	Temp.
0.20″	19°.78	9.20″	24°.22
1.20	19 .80	10.20	24 .22
2.20	19 .82	11.20	24 .22
3.20	19 .84	12.20	24 .215
4.20	Beginning of Expt.	13.20	24 .215
5.20	23 .54	14.20	24 .210
6.20	24 .10	15.20	24 .207
7.20	24 .19	16.20	24 .204
8.20	24 .21	17.20	24 .200

Therefore

$$\Sigma\Delta = \Big(23.54 + 24.10 + 24.19 + 24.21 + 24.22 + 24.22 + 24.22 + 24.215 + 24.215 + \frac{19.86 + 24.21}{2} - 10\times 19.82\Big)\left(\frac{0.003 + 0.02}{24.205 - 19.82}\right) - 10\times 0.02,$$

or

$$\Sigma\Delta = 0.015.$$

* Wüllner, Physik, 3, p. 407.

This correction has then to be added to the temperature observed at the end of the second period, or $\tau_{10}=24.210$, or

$$24.210+0.015=24°.225.$$

Another method for correcting for loss of heat due to radiation is to read the temperature of the calorimeter at short intervals of time, τ, after introducing the heated body until the maximum temperature has been reached. The fall of temperature in two or three minutes is then deter-

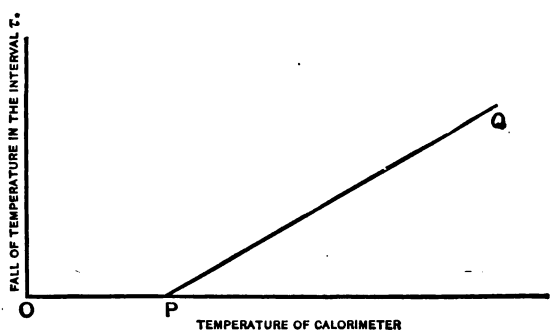

FIG. 41.

mined, and from this the fall in the interval τ calculated. In this way we ascertain the rate of cooling at the maximum temperature.

The rate of cooling is then determined at a number of temperatures between the maximum and the initial temperatures. A curve PQ is then drawn (Fig. 41) in which the temperatures of the calorimeter are plotted as abscissæ, while the fall in temperature at the different temperatures during the interval τ are plotted as ordinates.

The readings of the thermometer in the calorimeter while the thermometer was rising are plotted against times from the instant when the heated body was introduced. This

curve will have the form shown by (Fig. 42) the continuous line *DBC*.

From a point *N*, which corresponds to a time interval $\frac{\tau}{2}$, the ordinate *NR* is drawn. The temperature corresponding to *R* is then read from the axis of ordinates. From the curve in Fig. 43, the fall of temperature during the time τ when the calorimeter was at the temperature corresponding to *R* in Fig. 42 is then read off. This quantity is then added

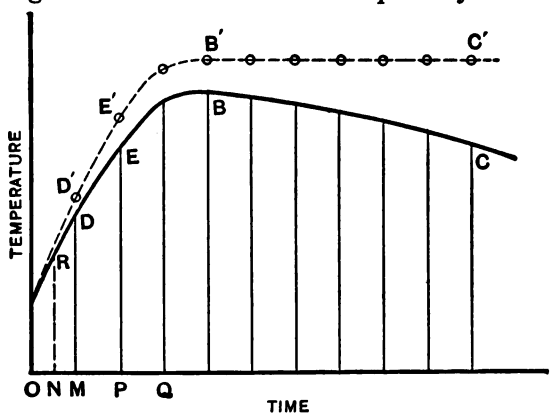

FIG. 42.

to the ordinate *MD*, giving a new point, *D'*, which represents what the temperature of the calorimeter would have been had there been no loss by radiation. In a similar manner the points *E'*, *B'*, etc., are obtained. From *B'* the curve remains horizontal, since if there had been no loss by radiation when the heated body and calorimeter had reached the same temperature, the temperature would have remained constant. The temperature corresponding to *B'* would therefore be the "corrected temperature."

(2) **Loss of Heat to Calorimeter.** — The water equivalent of the calorimeter is obtained by multiplying the weight of

the vessel by the specific heat of the material of which it is made. The table of specific heats on p. 82 will give the necessary data for such calorimeters as are usually employed.

(3) **Loss of Heat to Stirrer.**—The water equivalent of the stirrer is calculated in the same manner as that of the calorimeter. It should be noted, however, that only that portion of the stirrer which is immersed should be taken into account.

(4) **Loss of Heat to the Thermometer.**—The calculation of the water equivalent of the thermometer is complicated by the uncertainty as to the weights of the glass and mercury separately.

Fortunately, however, the heat capacities of glass and mercury for equal volumes are nearly equal. The specific heat of mercury = 0.034, and its density = 13.56. Its heat capacity = $0.034 \times 13.56 = 0.46$ per c.c. The specific heat of glass = 0.19, and its density = 2.4. Its heat capacity = $0.19 \times 2.4 = 0.46$ per c.c.

It is therefore only necessary to measure the volume of the bulb of the thermometer and multiply by 0.46 in order to obtain the water equivalent.

The determination of the volume is most easily made by weighing to centigrams a beaker partially filled with water, and then suspending in it the thermometer with the bulb immersed and observing the increase in weight of the beaker.

Determination of the Specific Heat of Liquids.—Probably the most accurate method for the determination of the specific heat of a liquid is that due to Pfaundler and Magie.* It consists in the comparison of the specific heat of a liquid in one calorimeter with that of the specific heat of another

* Magie, Phys. Rev., Vol. IX, No. 2, p. 65.

liquid chosen as a standard in another calorimeter. This comparison is made by observing the increase of temperature produced in each calorimeter when equal quantities of heat are supplied. These equal quantities of heat are produced by passing an electric current through two coils of the same resistance connected in series, each calorimeter being provided with one coil. By so proportioning the quantities of the liquids that the rise in temperature is identical in each calorimeter the usual calorimetric corrections may be neglected.

A section of one of the calorimeters is shown in Fig. 43. It consists of a cylindrical cup of thin brass four inches in diameter and six inches high. It is placed within a larger brass vessel six inches in diameter and eight inches high, and is centred by means of wooden pins projecting from the inner walls of the outer vessel. Through the wooden cover of the calorimeter pass two heavy copper wires, which are connected below the surface of the liquid by a German-silver resistance of nearly 4 ohms. The coil is held in position by a glass rod which projects downward from the cover. The heavy copper wires and the German-silver spiral are insulated by means of a varnish which resists the action of liquids. By means of a hot-air motor or a turbine the stirrers of the two calorimeters are operated, since inequality in stirring produces an appreciable error. The thermometer is inserted as shown, the bulb being about an inch below the surface of the liquid. The current for the coils is furnished by a dynamo or storage-cells, the circuit including a contact-maker, an ammeter, and a variable resistance. The current used should range from 4 to 5 amperes.

Method of Operation.—One calorimeter is filled with the standard liquid, usually 500 or 600 grams of water. The other calorimeter is filled with enough of the liquid of which

the specific heat is sought to give an equal rise in temperature. This must be determined by preliminary trials. The two calorimeters are cooled a few degrees below room tem-

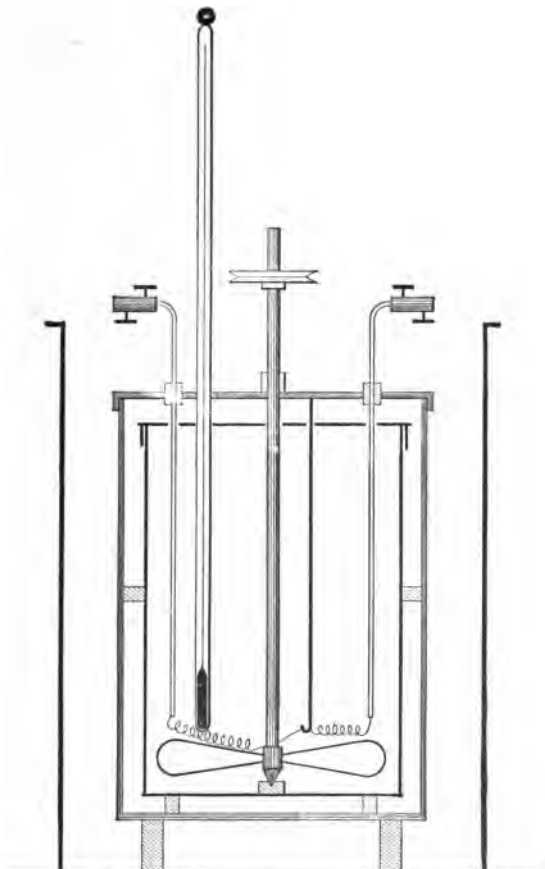

FIG. 43.

perature, and then placed in their respective positions and stirred. If the temperatures are not the same, the cooler vessel may be warmed with the hands. When the two cups

are within a few tenths of a degree of equality of temperature the current is switched on and the stirring started. The current is turned off when the temperature has risen as much above that of the room as it was below at the beginning of the experiment. The stirring is now continued and the thermometer observed until the maximum temperature is reached.

Let θ_1 = rise of temperature in water;
θ_2 = " " " " liquid;
m_1 = mass of water;
m_2 = " " liquid;
s = specific heat of liquid.

Then we have

$$m_1\theta_1 = m_2 s\theta_2,$$

or

$$s = \frac{m_1\theta_1}{m_2\theta_2}.$$

For further details the student should consult the original papers of Prof. Magie in the Physical Review, Vols. IX, XIV, and XVI.

Heat of Fusion.—The heat of fusion of a substance is the quantity of heat required to convert one gram of the substance from the solid to the liquid state without changing its temperature.

The molecular heat of fusion is the product of the molecular weight of the substance and the heat of fusion. The heat of solidification of a substance is the quantity of heat liberated when one gram of the substance is changed from the liquid to the solid state.

The molecular heat of solidification is the product of the molecular weight of the substance and the heat of solidification.

Since substances after solidifying are not always in the same molecular condition, there are often considerable differences between the heats of fusion and solidification. Whenever possible it is preferable to determine the heat of fusion rather than the heat of solidification.

The method usually employed is Regnault's method of mixtures (p. 78).

(1) *Heat of Fusion.*—If the substance melts below the temperature of the room, it is introduced into the calorimeter in the solid state and allowed to melt. The calorimeter is provided with enough liquid so that the final temperature shall be above that of the melting-point of the substance.

The total quantity of heat lost by the liquid in the calorimeter is the sum of three quantities, as follows:

(1) The quantity of heat taken up by the substance in passing from the initial temperature of the liquid in the calorimeter to that of the melting-point of the substance.

(2) The quantity of heat required to melt the substance.

(3) The quantity of heat required to heat the melted substance to the final temperature of the liquid in the calorimeter.

Let L = heat of fusion of the substance;

T = temperature of substance when introduced into calorimeter;

M = mass of substance;

S = specific heat of solid substance;

S_l = specific heat of liquid substance;

m = mass of liquid in calorimeter (usually water);

s = specific heat of liquid in calorimeter (for water = 1);

t_1 = initial temperature of liquid in calorimeter;

t_0 = melting temperature of substance;

t_2 = final temperature of liquid in calorimeter;
w_1 = water equivalent of vessel containing substance;
w_2 = water equivalent of calorimeter and accessories.

Then the quantity of heat given up by the calorimeter and its contents will be $(m+w_2)(t_1-t_2)$, and the quantity of heat absorbed by the substance and vessel will be

$$M[S(t_0-T)+L+S_l(t_2-t_0)]+w_1(t_2-T).$$

Equating these two expressions and solving for L, we get

$$L=\frac{(m+w_2)(t_1-t_2)-w_1(t_2-T)-M[S(t_0-T)+S_l(t_2-t_0)]}{M}.$$

(2) *Heat of Solidification.*—Should the melting-point of the substance be above that of the temperature of the room, then the heat of solidification is obtained.

A moment's reflection will make it clear that the method is exactly the reverse of that given above. Denoting the heat of solidification by E, the formula for this quantity can be shown to be

$$E=\frac{(m+w_2)(t_2-t_1)-w_1(T-t_2)-M[S_l(T-t_0)+S(t_0-t_2)]}{M}.$$

Method of Operation.—The substance in either the solid or the liquid state is introduced into the calorimeter in a small platinum or silver bottle.

The specific heats of the solid and liquid substances are ascertained for the interval of temperature of the experiment. The experimental details are exactly similar to those in the determination of specific heat (p. 82).

The heat of fusion may be calculated approximately from the molecular depression of the freezing-point for the substance as a solvent.

If L is the heat of fusion of the solvent, T its freezing-

point in absolute temperature, and Δ its molecular depression, then

$$L = \frac{0.02T^2}{\Delta}.$$

Heat of Vaporization.—The heat of vaporization is the quantity of heat required to convert one gram of a liquid at its boiling-point into vapor at the same temperature.

The molecular heat of vaporization is the product of the molecular weight of the substance and the heat of vaporization. There is no difference in value between the heat of vaporization and the heat of condensation.

The method employed in the measurement of this quantity consists in vaporizing a definite quantity of liquid and condensing the vapor in a calorimeter.

Let V = heat of vaporization;
M = mass of liquid converted into vapor;
T = boiling-point of liquid;
t_2 = final temperature of water in calorimeter;
S = mean specific heat of liquid between T and t_2;
m = mass of water in calorimeter;
w = water equivalent of calorimeter and accessories;
t_1 = initial temperature of water in calorimeter.

Then the quantity of heat given up by the vapor in condensing to a liquid in the calorimeter is $M[S(T-t_2)+V]$, and the quantity of heat taken up by the calorimeter and contents is $(m+w)(t_2-t)$.

Equating these two expressions and solving for V, we have

$$V = \frac{(m+w)(t_2-t_1)-MS(T-t_2)}{M}.$$

Apparatus and Method.—The method here described is Kahlenberg's modification of Berthelot's method.* The

* Kahlenberg, Jour Phys. Chem Vol 5 No 4. p 215

main difference between this new apparatus and that devised by Berthelot lies in the construction of the retort. The construction of the apparatus is shown in Fig. 44, the

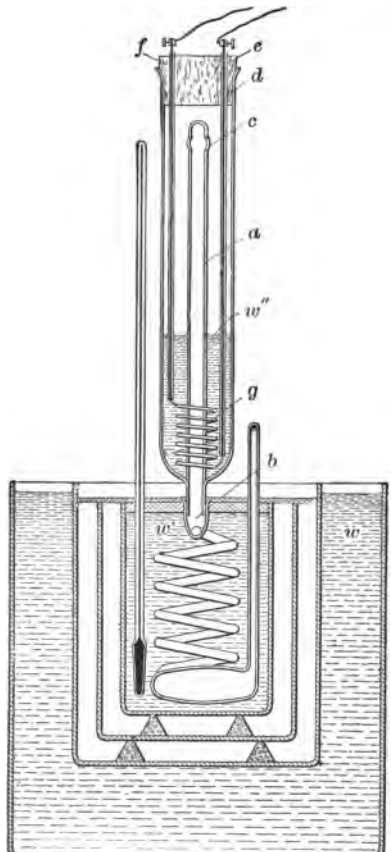

FIG. 44.

retort being represented rather large in proportion to the rest of the apparatus in order to show the details. The retort where the liquid is heated consists of a test-tube 17 cm.

long and 3.5 cm. in diameter, into the bottom of which is fused the tube *a*, which fits into the condenser with a ground-glass joint at *b*. At *c* there are two large lateral openings. The glass tubes *e* and *f* pass through a good cork, *d*. Into these tubes are fused the ends of the spiral of platinum wire *g*. This spiral consists of about 40 cm. of stout platinum wire, to the ends of which are welded short heavy pieces of platinum rod; and these rods in turn are fused into the glass tubes. Long, rather heavy copper wires pass down the glass tubes at the bottom of which they are connected with the ends of the platinum rods by means of a few drops of mercury. Two small binding-screws serve to connect the copper wires with the ends of other wires that lead to the source of electricity, as indicated in the illustration.

It is obviously essential that the lower end of the tube of the retort which connects with the condenser at *b* be made so short as to prevent premature condensation of the vapors in this part of the tube. In the figure this protruding part of the tube has been represented rather longer relatively than it ought to be.

The calorimeter is covered with a heavy piece of asbestos board coated with tin-foil and shaped so as to fit snugly. The small space between the bottom of the retort and the cover of the calorimeter is nicely packed with cotton, and in fact the whole retort is inclosed in cotton during the progress of the experiment, a few peep-holes being left through which the boiling may be observed. This cotton covering of the retort which has not been represented in the figure serves very effectively to screen the thermometer and calorimeter from the hot retort; at the same time it prevents the latter from becoming chilled, thus materially aiding the progress of the experiment. This screen can be made very easily by gluing a layer of cotton batting on thin asbestos

paper. By placing the screen so as to rest on the calorimeter-cover it may be bent so as to inclose the retort, remaining in position without any further support. The calorimeter, of about 1250 c.c. capacity, is made of very thin nickel-plated sheet copper. It is somewhat elliptical in shape, thus permitting the thermometer to be placed at a greater distance from the retort than would be possible by using a vessel of the same capacity but of circular cross-section. The stirrer, which is not represented in the figure, is made of thin copper. It is provided with a hard-rubber handle, by means of which an up-and-down motion is imparted to it. The thermometer employed is of the Beckmann type. The condenser is made of glass. A current of from 8 to 15 amperes, according to the nature of the liquid under investigation, is sufficient to heat the liquid to boiling.

This current is taken either from a dynamo or from twelve or more large storage-cells, representing an E.M.F. of about 24 volts. A rheostat placed in the circuit permits the current to be adjusted as desired, the strength of the latter being indicated by an ammeter.

The liquids are brought to boiling rather slowly, but are kept boiling vigorously when once ebullition has started. The boiling is usually continued for about five minutes, care being taken not to evaporate the liquids so far as to expose the platinum spiral. The amount of liquid evaporated is ascertained by weighing both the retort and condenser on an analytical balance before and after the experiment. The weights thus obtained act as a check upon each other; they generally agree to within a few centigrams. The average of these two weights is taken. The loss of heat due to radiation during the experiment is corrected by the method of Regnault-Pfaundler given on p. 82.

In Fig. 45 is shown a simpler form of retort, also devised

by Kahlenberg. Here the test-tube is inverted, the lower end being closed with a good rubber stopper, through which the glass tube passes, connecting with the condenser as indicated. The ends of the spiral of platinum wire are welded to rather heavy platinum rods, which pass through the rubber stopper as shown in the figure. The ends of these rods are connected with the wires leading to the source of

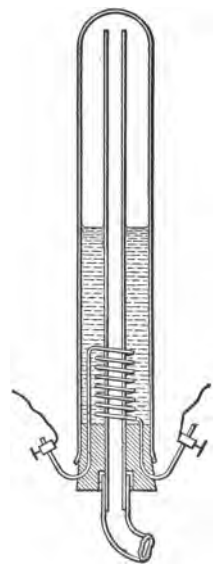

FIG. 45.

electricity by means of small binding-screws. This form of the retort is much simpler than that in Fig. 40, and it is consequently to be preferred whenever the liquid tested does not attack the rubber stopper. Rubber being a poor conductor of heat, the stopper itself serves to screen the calorimeter from the hot liquid in the retort. The heat of vaporization may also be calculated from the elevation of

the boiling-point in the same manner as the heat of fusion is calculated from the depression of the freezing-point.

The formula is

$$V = \frac{0.02T^2}{\rho},$$

where V is the heat of vaporization, T the absolute temperature at which the liquid boils, and ρ is the molecular elevation of the boiling-point for the liquid as a solvent.

A very interesting relation between molecular heats of vaporization and absolute boiling temperatures has been pointed out by Trouton. This rule states that *the molecular heats of vaporization are proportional to the absolute temperatures at which the liquids boil.* This may be formulated thus:

$$\frac{M_h}{T} = \text{constant}.$$

That it certainly holds for a large variety of substances has been shown by Ostwald and others.*

Thermochemistry. — In all thermochemical measurements it is found convenient to employ as a unit the large calorie, which is one hundred times the small calorie. The large calorie, then, is nearly equal to the quantity of heat required to raise 1 gram of water from 0° to 100°.

The results of thermochemical measurements are always expressed in terms of gram-molecular weights.

The notation employed is that due to J. Thomsen.

The following examples will serve to illustrate the method of expressing the results:

$$H_2 + O = H_2O + 68{,}360 \text{ cals.},$$

or

$$[H_2, O] = 68{,}360 +.$$

* Phil. Mag., **18**, 54 (1884); Liebig's Ann., **234**, 338 (1886); Ostwald's Lehrbuch d. allg. Chem., **1**, 335.

Either of these equations means that when 2 grams of hydrogen unite with 1 gram of oxygen to form 18 grams of water 68,360 calories of heat are set free.

In the same manner

$$NH_3 + HCl = NH_4Cl + 41{,}900 \text{ cals.},$$

or

$$[NH_3,\ HCl] = 41{,}900+,$$

expresses that 41,900 calories of heat are liberated when one gram-molecule of ammonium chloride is formed from one gram-molecule of ammonia and one gram-molecule of hydrochloric acid.

The plus sign shows that the reaction is exothermic. Should the reaction be endothermic, a minus sign would express the fact.

If the reaction takes place in the presence of a large quantity of water, the equation is written

$$KOH\ aq. + HCl\ aq. = KCl\ aq. + 13{,}700 \text{ cals.},$$

where the symbol *aq.* shows that the potassium hydroxide, the hydrochloric acid, and the potassium chloride are each in solution.

If it is desired to represent the heat liberated when a substance dissolves in water, the symbol *aq.* is written after the formula of the substance, thus:

$$HCl,\ aq. = 17{,}320.$$

This means that when one gram-molecule of hydrochloric acid dissolves in water 17,320 calories of heat are set free.

If both chemical action and solution are to be represented, the equation is written

$$H + Cl + aq. = HCl + aq. + 39{,}300.$$

This expressed in words is that when one gram-molecule of hydrogen combines with thirty-five and four-tenths grams of chlorine in the presence of water the heat liberated due to combination and solution is 39,300 calories.

The state of aggregation of the reacting substances and of the resulting products is commonly expressed by means of the type. The gaseous state is represented by italics, the liquid by ordinary type, and the solid by extra-heavy type, thus:

H_2O..... water vapor
H_2O..... liquid water
H_2O..... ice.

The most important of the thermochemical laws are:

(1) *Law of Lavoisier and Laplace.*—The amount of heat which is required to decompose a compound into its constituents is exactly equal to that which was evolved when the compound was formed from these constituents.

(2) *Laws of Hess.*—(*a*) The heat evolved in a chemical process is the same whether it takes place in one or in several steps.

(*b*) If two salt solutions which are nearly completely dissociated are mixed, no thermal change occurs, provided the ions do not unite to form molecules.

(3) *Laws of Berthelot.*—(*a*) The thermal change in a chemical reaction, if no work is done, depends only upon the condition of the system at the beginning and at the end of the reaction, and not on the intermediate conditions.

(*b*) The heat evolved in a chemical process is a measure of the corresponding chemical and physical work.

(*c*) Every chemical transformation which takes place without the addition of energy from without, tends to form that substance or system of substances, the production of

which is accompanied by the evolution of the maximum amount of heat.

For a discussion of these laws and a fuller treatment of the subject of thermochemistry the student must consult a text-book of physical chemistry.

Heat of Neutralization.—When an acid is neutralized by a base heat is set free. The amount of heat liberated when one gram-molecule of an acid reacts with one gram-molecule of a base, in dilute solution, is called the *heat of neutralization.*

Apparatus and Method of Operation.—The apparatus used is a modification of that devised by Thomsen. The main points of it are shown in Fig. 46.

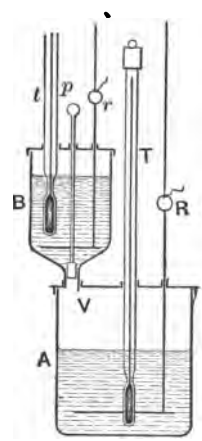

FIG. 46.

A and *B* are two cylindrical vessels having respective capacities of 1000 and 500 c.c. The vessels may be made of nickel-plated brass. The vessel *B* communicates with *A* through the valve *V*, which can be opened by means of the handle *p*.

Both A and B are provided with stirrers r and R, and with insulating covers which are perforated to admit the thermometers and stirrers. The two vessels are provided with outer cylinders of polished brass (not shown in figure) to insure insulation.

The thermometers used are of the Beckmann type graduated to $\frac{1}{5}\frac{1}{0}$ or $\frac{1}{10}\frac{1}{0}$ of a degree.

The thermometers should be compared frequently by observing the temperatures indicated by each when immersed in the same liquid.

The rules already given for the use of a calorimeter are to be applied in the use of this apparatus. The solutions used should be very dilute; usually one gram equivalent of acid or base in two hundred gram-molecules of water.

It will be found convenient to have an exact submultiple of the molecular weight of the solution in the calorimeter. For a solution of $NaOH+100H_2O$ (molecular weight 1840 grams) one-fourth or one-sixth of a gram molecule is used; the solution would then contain 450 or 300 grams of water.

In the same manner for an equivalent solution of sulphuric acid, $\frac{1}{2}H_2SO_4+100H_2O$, one-fourth or one-sixth equivalent should be placed in the calorimeter. It is obviously a matter of indifference which vessel contains the acid and which the base.

The solutions should be thoroughly stirred and the thermometers carefully noted. When the temperatures have remained constant for several minutes the thermometers are read and the valve V opened. The establishment of thermal equilibrium takes only a very short time (usually one minute). The measurements should be made at room temperature (18° to 20°). If the change in temperature after mixing is not more than 1°, no radiation correction need be applied.

Let $M_1 = M_2$ be the weights of water in the two solutions;
t_1 be the temperature of the solution in vessel containing M_1 grams of water;
t_2 be the temperature of the solution in vessel containing M_2 grams of water;
θ be the final temperature after mixture;
w be the total water equivalent;
$\frac{1}{m}$ be the fraction of a gram-molecule which is contained in the solutions;
N be the heat of neutralization for one gram-molecule expressed in large calories.

Then we have

$$N = \frac{m}{100}\{M_2(\theta - t_2) + (M_1 + w)(\theta - t_1)\}.$$

This formula assumes the specific heat of the solutions to be unity, which is permissible for very dilute solutions.

Heat of Solution.—The heat evolved or absorbed by the solution of one gram-molecule of a substance in a definite number of molecules of solvent is known as the *heat of solution.*

Apparatus and Method of Operation. — The apparatus employed is the mixture-calorimeter. All of the precautions which were given under the determination of specific heat must be observed here.

It is advisable to have a fractional part of the molecular weight of the solution in the calorimeter, as in determining the heat of neutralization.

$\frac{1}{m}$ gram-molecules of the solute is weighed out, and M grams of water are weighed in the calorimeter. Denoting by w the total water equivalent and letting t and θ denote the

initial and final temperatures, the heat of solution S is given, in large calories, by the formula

$$S=\frac{m}{100}(M+w)(\theta-t).$$

Here, as in the formula for heat of neutralization, the specific heat of the solution is assumed to be unity. In order that both solute and solvent may acquire the common temperature t, the weighed quantity of solute is sealed in a thin gla s bulb and introduced into the water. When the temperature has become uniform the bulb is broken by means of the stirrer. The accuracy of the results depends upon the time required for complete solution.

Should the final temperature vary more than three degrees from that of the room, the correction for radiation must be applied.

The method given above is obviously only applicable to solids and liquids. To determine the heat of solution of gases the gas is bubbled through the water in the calorimeter, the size of the bubbles being regulated according to the solubility of the gas. The solution in the calorimeter is then analyzed and thus the quantity of gas dissolved is determined. The arrangement of apparatus for determining the heat of solution of a gas is shown in Fig. 47. If it is desired to determine the heat of solution of a salt containing water of crystallization, care should be taken to have the quantity of water in excess of that present in the salt, otherwise the salt will lose water of crystallization.

If the salt contains n molecules of water of crystallization, $200-n$ or $400-n$ molecules of water are chosen as solvent. Thus, for $MgSO_4+7H_2O$, 393 molecules of water would be used as solvent. Since the heat of solution is numerically equal to the heat of precipitation, the former

may be measured by the latter. To measure the heat of solution from the heat given out in the precipitation of a gram-molecule of solute it is necessary to (1) form the substance in the solution at such a dilution that no precipitation occurs, and (2) so that precipitation is complete. The dif-

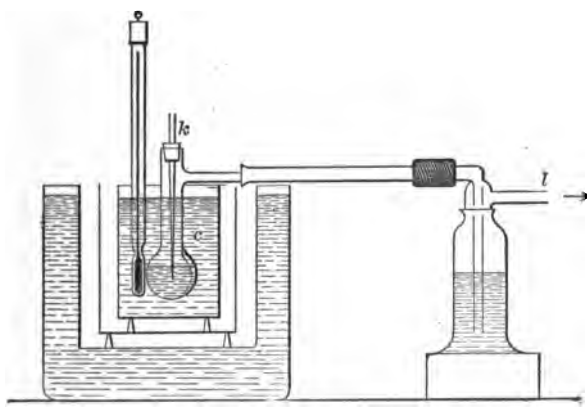

FIG. 47.

ference between these two heat values is the heat of solution sought.

Heat of Hydration.—The quantity of heat liberated when one gram-molecule of a salt combines with a definite number of molecules of water to form a hydrate is known as the *heat of hydration.*

The heat of hydration is obtained by subtracting the heat of solution of the hydrated salt from the heat of solution of the anhydrous salt.

The method for the determination of the heat of hydration is thus that for the heat of solution. If it is desired, for example, to obtain the heat of hydration when $CaCl_2+6H_2O$ is formed from $CaCl_2$, we measure (1) heat of solution of $CaCl_2=S_1$, and (2) heat of solution of $CaCl_2+6H_2O=S_2$.

The thermal effect in the first process consists of two parts: (*a*) the heat of hydration of $CaCl_2$ (positive thermal effect), (*b*) the heat of solution of $CaCl_2+6H_2O$ (negative thermal effect).

The thermal effect in the second process consists of the thermal effect $CaCl_2+6H_2O$, aq. The heat of hydration H is

$$H=S_1-S_2.$$

The thermal effects for the combination with the first, second, third, etc., molecules of water are usually quite different. For this reason it is advisable to determine the heats of hydration for 1, 2, 3 . . . n molecules of water of crystallization. The salts are dehydrated in an ordinary drying-oven. The directions given on p. 104 should be followed in making up the solutions.

Heat of Dilution.—The thermal change which is caused by the dilution of a solution with the solvent is known as the *heat of dilution.* The quantity of water of the solution and the ultimate quantity of water are ordinarily so chosen that the total quantity is a constant. Thus HCl 50 aq., 50 aq., HCl 25 aq., 75 aq., HCl 30 aq., 70 aq., etc., or in general HCl n aq., $100-n$ aq.

The heat of dilution is best determined in the mixture-calorimeter, the process being nearly analogous to that for the determination of the heat of solution. The solution to be diluted is introduced into the calorimeter in a small, closed glass vial; when the temperature has become uniform the vial is broken and the thermal change noted.

Let t_w = the initial temperature of the water;
t_s = the initial temperature of the solution;
θ = final temperature of the mixture;
c = specific heat of the mixture;
w = water equivalent of calorimeter and accessories;

M_w = mass of the water;
M_s = mass of the solution to be diluted;
$\frac{1}{m}$ = fraction of a gram-molecule of solute contained in solution;
D = heat of dilution.

Then the heat of dilution in large calories is

$$D = \frac{m}{100}\{(\theta - t_s)\,[(M_w + M_s)c + w] - (t_w - t_s)(M_w + w)\}.$$

The loss of heat due to radiation must be taken into consideration.

The specific heats of solutions may be found in the Tables of Landolt and Börnstein, p. 185, 1883.

Heat of Combustion.—The quantity of heat liberated when one gram-molecule of a substance is completely burned is known as the *heat of combustion.*

The substance of which the heat of combustion is to be determined is placed in a specially designed vessel, which is then filled with oxygen under definite pressure. The vessel, which is known as the calorimetric bomb, is introduced into a calorimeter and the substance is then burned, the heat liberated being absorbed by the water in the calorimeter.

Let t = initial temperature of calorimeter;
θ = final temperature of calorimeter;
M = mass of water in calorimeter;
w = total water equivalent of calorimeter;
m = mass of substance burned;
p = molecular weight of the substance;
C_v = heat of combustion at constant volume;
C_p = heat of combustion at constant pressure.

Then we have

$$C_v = \frac{p}{100m}(M + w)(\theta - t)$$

and

$$C_p = C_v + 0.02qT,$$

where q denotes the number of gram-molecules of gas which disappear in the reaction, and T denotes the absolute temperature.

The reduction of the heat at constant volume to heat at constant pressure at 18° for solids and liquids of the formula $C_xH_yO_z$ is made by the formula

$$C_p = C_v + 0.291\left(\frac{y}{2} - z\right).$$

Apparatus.—The apparatus here described is the Atwater* modification of the Berthelot bomb calorimeter. The apparatus consists of:

(1) The calorimeter proper, including the bomb, a britannia-metal cylinder to hold the water in which the bomb is immersed, a thermometer and a stirrer.

(2) Two concentric protecting cylinders of "indurated fibre" with cover. These inclose the calorimeter system and insulate it.

(3) Accessory apparatus, including appliances for filling and closing the bomb, electric devices for igniting the substance, and mechanism for operating the stirrer.

The Bomb.—The bomb consists of three parts: A cylindrical cup to contain the substance to be burned and the oxygen for combustion, a cover to close the cup, and a threaded ring or collar to hold the cover tightly on the cylinder. With these is a metal capsule to hold the substance. The parts are shown assembled in Fig. 48. The cup is of the best tool-steel, as are also the cover B, collar C, and the screws E, F. The approximate dimensions of the cup are:

* Atwater and Snell, Jour. Am. Chem. Soc., **25**, 659, 1903.

Depth, 13 cm.; diameter, 6 cm. at top and 5.5 cm. at bottom. The wall is a little over 0.5 cm. in thickness. The weight is about 3 kg., and the capacity a little over 350 c.c.

The cover is lined on the bottom, and is provided with a neck, *D*. Into this fits, at the top, a cylindrical screw, *E*,

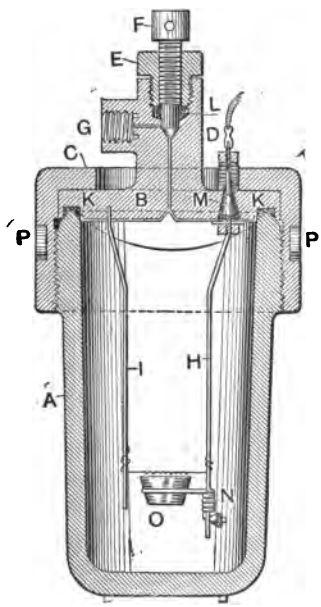

FIG. 48.

into which in turn fits a valve-screw, *F*. In the neck *D*, where the bottom of the cylindrical screw *E* rests, is a shoulder fitted with a packing of lead, *L*. The pressure of the valve-screw on this packing makes a tight closure upon the part of *F* which it surrounds. On the side of *D* is an opening, *G*, into which may be screwed the coupling connecting the tube with the receptacle which holds the oxygen used for the combustion.

The coupling when screwed in thrusts against a washer of lead at the end of *G* which insures perfect closure. A narrow passage runs horizontally to a point just above the valve-seat in the centre of *D*. A similar passage runs from the apex of the valve-seat perpendicularly downwards through the cover.

These two passages provide a channel for the oxygen to pass into the interior of the bomb.

This channel may be tightly closed by the valve-screw, the lower end of which is conical and thrusts against the inner surface of *D*, the angle of which at the place of contact corresponds to that of the tip of the screw. Between the top of the valve-seat and the bottom of the packing *L* the valve-screw fits so closely in the cover as to prevent the lead of the packing from working downward and thus obstructing the small gas-passages.

The upper edge of the cup *A* is bevelled on both sides; the apex is rounded and fits into a gasket, *K*, of lead, which is held in a groove in the cover *B*. The platinum wires *H* and *I* inside the bomb serve to hold the capsule *O* containing the substance to be burned and to conduct an electric current for igniting it. Of these two wires, one, *I*, is screwed into the cover; the other, *H*, passes through a conical hole and is insulated from the metal. Near the lower end of *H* is a platinum wire bent in the form of a ring to hold the capsule, and coiled about the wire, to which it is held by a platinum thumb-nut. When a combustion is made the two platinum wires are connected by a very fine iron wire which passes over the capsule and is heated by the electric current. The part directly above the substance to be burned is wound into a spiral, thus furnishing a larger quantity of iron to be ignited and, falling, to ignite the substance in the capsule.

The cup and the cover are lined with gold-plated copper.

The lining of the cup is made from a single sheet of metal, which is spun to fit the steel cup accurately. It can be easily removed from the latter by placing the fingers of the left hand inside the lining, and the thumb against the threads of the cap, and drawing outward upon the lining, at the same time tapping the steel cup with a wooden mallet.

The sample for combustion is held in a metal capsule which is supported in the bomb as shown in Fig. 44. The capsule is made of sheet nickel 0.4 mm. in thickness. It is 1.7 cm. deep, 1.5 cm. in diameter at the base and 2.2 cm. in diameter at the top.

The ignition of the sample is effected by means of a small coil of iron wire heated to ignition by an electric current.

The thermometer used is of the ordinary Beckmann type, graduated to $\frac{1}{100}$ of a degree.

When ready for a combustion the bomb is immersed in water contained in a small metal cylinder.

This cylinder is surrounded by concentric cylinders of 'ndurated fibre, leaving air-spaces to prevent undue passage of heat between the water and the outer air. The assembled apparatus is shown in section in Fig. 49. The cylinder is of Britannia metal, 13 cm. in diameter, 23 cm. high, and holds with the bomb not far from 2 litres of water. A stirrer, *SS*, moved by a small motor keeps the water in motion and insures the mixture needed for equalizing its temperature. The stirrer consists of two perforated annular pieces of sheet brass connected by two brass rods which project out of the calorimeter and are there attached by thumb-screws to a nickel-plated cross-piece. A groove is cut in one side of the annular pieces to admit the thermometer. The calorimeter stands on cork supports which prevent it from coming in contact with the bottom indurated-fibre

vessel. The diameters of the indurated-fibre vessels *U* and *T* are such as to leave an air-space of about 1 cm. between

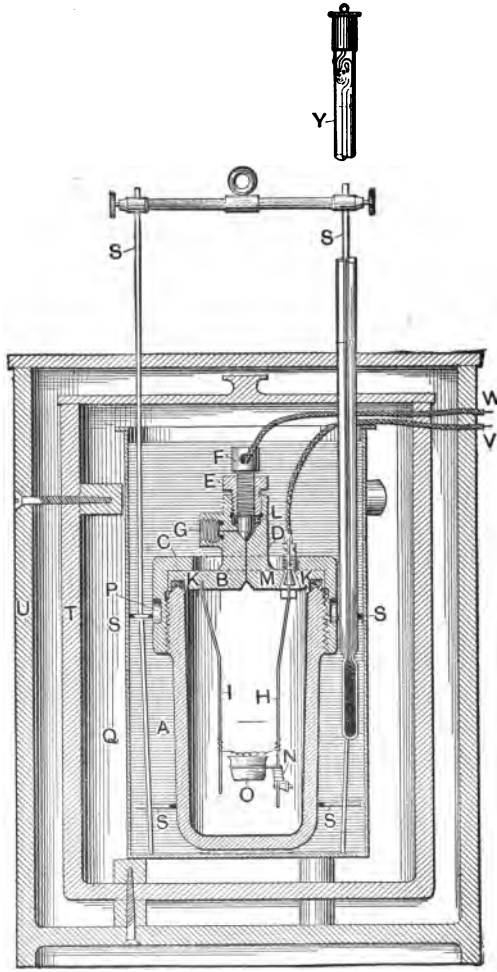

FIG. 49.

the two vessels and one of 3 cm. between the inner vessel and the calorimeter cylinder. The covers of the vessels are

of hard rubber. They are provided with holes for two rods of the stirrer and the thermometer.

Accessory Apparatus. — The stirring-apparatus may be operated either by a small hot-air engine of $\frac{1}{20}$ horse-power, or a small electric motor of the same power. The substance is ignited by means of a current of from 3 to 4 amperes, which may be obtained from the 110-volt street current by sending it through four 32-candle-power, 110-volt lamps in parallel. The substance to be burned, if in the solid state, is usually pressed into small pellets in a pellet-press. The oxygen used is obtained in steel cylinders, each of which should contain enough oxygen for 250 determinations. Brass coupling-tubes serve to connect the cylinder with a manometer and the bomb. By means of the manometer one can tell when the supply of gas is nearly exhausted.

General Test of the Apparatus.—"The general condition of the apparatus should be tested from time to time by check combustions. Benzoic acid and cane-sugar are convenient substances for this purpose, because they are easily obtained pure and their heats of combustion are accurately known." "The benzoic acid has the advantage over the sugar that the pellets do not clog the pellet-mould and that no kindler other than the iron wire is needed for the ignition."

METHOD OF USE OF THE APPARATUS.—*Quantity of Substance to be Used.*—"The quantity of material burned in the bomb should be such as will yield from 4000 to 7000 calories."

"Of substances which have been found convenient for tests of the accuracy of the determinations, the following are suitable quantities:

Naphthalene and camphor	0.5 to 0.7 gram
Benzoic acid and hippuric acid	0.7 to 1.0 gram
Cane-sugar and glycocoll	1 to 2.0 gram."

Preparation of the Material for Combustion.—Solids. "Solids in general are powdered and pressed into cylindrical pellets in the pellet-mould as described above. The material is weighed approximately before, and accurately after, moulding."

"With some substances special devices are required to secure ignition. A crystal of naphthalene serves as a kindler for such substances as sugar and glycocoll. The naphthalene may be inserted between two turns of the coiled iron wire with one edge touching the substance in the capsule. Or, instead of a coil, the wire may be formed into a loop resembling one of the forms of wire office-clips used for holding sheets of paper together, and the naphthalene placed in the loop, which should touch the substance in the capsule."

"Substances which are still more difficult to ignite, e.g., creatin and creatinin, may be enclosed in gelatin capsules, such as are used with volatile liquids (see below)."

Oils.—"Oils are absorbed in fibrous asbestos. The metal capsule is half-filled with asbestos, ignited in a Bunsen flame, cooled in a desiccator and is weighed before and again after addition of the oil."

Volatile Liquids.—"Volatile liquids, e.g., alcohol, may be enclosed in gelatin capsules. We have found the 'Beekman ideal' capsule No. 00, which weighs from 0.11 to 0.19 gram, very convenient for the purpose."

Filling the Bomb.—"The bomb-cover being supported upon a ring-stand, the capsule containing the pellet is placed in position in the platinum ring. The ends of the coil of iron wire are wound around the vertical platinum wires (one turn only) and the coil adjusted so that it touches the substance to be burned, but not the capsule. The naphthalene (if any is to be used) is placed in position. The cover is now placed on the bomb and a little oil dropped upon the top to

prevent its turning with the collar, which is then screwed on and tightened by means of a clamp and spanner. The bomb is now ready to be filled with oxygen. With its valve slightly open it is placed in position on an iron shelf and connected with the manometer, which is kept permanently connected with the oxygen cylinder. The valve of the oxygen cylinder is then opened cautiously. When the manometer indicates a pressure of 20 atmospheres the oxygen is cut off, the bomb-valve closed, and the bomb disconnected from the manometer."

"Leakage of gas from the bomb may occur either at the soft-metal gasket (*K*) or at the conical tip of the valve-screw (*F*) (Fig. 48). Gas escaping at the gasket will usually make an audible sound. If the gasket is not too much worn, the leak may be stopped by screwing the collar tighter. A leak at the valve can be easily and quickly detected by placing the moistened finger over the opening (*G*). When the valve-tip or the conical shoulder into which it fits becomes corroded so that the valve cannot be closed by gentle pressure, it must be reseated carefully in a lathe to secure a proper fit. If, in filling the bomb, leakage occurs at *L* (Fig. 48), the cylindrical screw (*E*) should be tightened a little to press the packing (*L*) tightly around the valve-screw."

Arranging Apparatus for the Combustion.—"The calorimetric water should now be put in the Britannia-metal cylinder. Both the quantity and the temperature of this water are to be regulated. In order to facilitate the calculations, it is better to make the quantity always the same and such that the total hydrothermal value of the calorimeter system will be a round number, such as 2000, 2100, or 2200 grams. In order to reduce to a minimum the correction for the influence of the surroundings upon the temperature of the system, the water in the cylinder should be made cooler

than the surroundings of the system (as measured by an ordinary thermometer placed in the inner air-space) by about the expected rise in temperature, or a little more. For example, if the quantity of substance to be burned is such as will yield about 6300 calories and the hydrothermal value of the system is to be 2100 grams, the rise expected will be 3° and the water in the cylinder should be made 3°–3.2° cooler than the air of the inner air-space. The insertion of the bomb, which is at room temperature, will decrease this temperature difference by about one-sixth, the hydrothermal value of the bomb being about one-sixth that of the whole system, so that after the combustion the temperature of the system will be a little above that of the surroundings."

"It is, obviously, more convenient to adjust the temperature of the water first and the quantity afterwards. The desired temperature can be readily obtained by mixing cooler water with that used in the preceding combustion (or with a portion of it). Water is then poured out of the cylinder until approximately the desired quantity remains; the cylinder, containing water and stirrer, is placed upon a tared balance, accurate to 1 gram, and small quantities of water are added or removed until the correct weight is obtained. The tare required is, of course, the desired hydrothermal value (e.g., 2100 grams) minus the hydrothermal equivalent of the apparatus and plus the weight of the cylinder and stirrer."

"The cylinder, containing stirrer and water, is now put in place inside the outer cylinders and the two conducting wires are joined, respectively, to the valve-screw and to the insulated conductor. The covers are put on and adjusted so that the stirrer will run smoothly, the thermometer is inserted and the stirrer set in motion. As soon as the different parts of the calorimeter system have assumed a common

temperature, which usually requires two or three minutes, the mercury will begin to rise at a uniform rate, and the readings of the 'initial' or precombustion period may begin."

"The room temperature may have changed so much since the apparatus was last used that the thermometer must be reset. In that event the water should be stirred a little after the insertion of the bomb and its temperature determined with an ordinary thermometer, so that the actual temperature to which the zero of the reset thermometer corresponds may be known within half a degree."

Temperature Changes in the System.—"If the calorimeter system were absolutely insulated thermally, only two temperature observations would be necessary for the determination of the heat of combustion of the substance. One of these could be made at any time after the system had come to internal temperature equilibrium after the insertion of the bomb, and before the ignition of the substance, for the temperature would remain absolutely constant during this interval of time whatever might be its length. This observation would give the initial temperature of the system. The second observation, that of the final temperature, could be made at any time after the heat from the combustion had distributed itself uniformly throughout the system, for then the temperature would again remain constant."

"But it is of course impossible to insulate the system completely and, consequently, external influences are continually affecting its temperature. The most obvious and doubtless the most important of these external influences is the temperature of the medium surrounding the system. This medium may be regarded as made up of (1) the air of the inner jacket; (2) the walls of the inner indurated-fibre cylinder; and (3) the air and walls of the outer air-jacket and the air of the room. Interchange of heat occurs be-

tween the system and (1) the air of the inner air-jacket, by convection and radiation; (2) the indurated-fibre cylinder by radiation; and (3) the air of the outer air-jacket and of the room by conduction through and convection by the rods of the stirrer. All of these interchanges may be fairly assumed to obey Newton's Law."

"The correction for the 'external influences' may, therefore, be estimated on the assumption that the rate of warming or cooling of the calorimeter system in a given minute is proportional to the difference between the average temperature of the system for that minute and the temperature of the surrounding medium. Further, the temperature of the surrounding medium may be regarded as constant. The correction for the effect of external influences on the temperature of the system may, therefore, properly be determined according to the method of Regnault, which is based upon the assumptions just mentioned."

The Thermometer Readings.—"Readings may be begun at any time after the stirrer has been set in motion. They should be continued until there has been a *uniform* rise of temperature for five minutes, the differences between successive readings not varying by more than 0.002°. These five minutes constitute the initial or precombustion period.

"Precisely at the end of the five minutes (i.e., at the sixth reading of the initial period) the electric circuit through the fine iron wire in the bomb is completed by closing a switch. The resistance-lamps are incandescent during the passage of the current, and the extinction of their light indicates that the iron wire has been fused. This usually occurs within two or three seconds after the closing of the circuit. The switch should now be opened immediately to avoid error from the production of heat in the calorimeter by the passing of the current through the water.

"Readings should be continued at intervals of one minute

until the rate of fall of the mercury has become regular—an indication that internal equilibrium has been regained. This marks the end of the combustion period. In routine work, however, it is convenient, for the sake of uniformity in the calculations, to regard the combustion period as ending, in all cases, five minutes after the ignition. After the final reading of the combustion period the stirring is continued for five minutes (final or 'postcombustion' period), at the end of which time another reading is taken.

"Before each reading the thermometer should be tapped with the electric hammer."

After the Combustion. — "The bomb is now removed from the calorimeter and placed in the clamp. After the pressure has been relieved by opening the valve, the collar is unscrewed and the cover removed. The interior of the bomb and the lining of the cover are rinsed with water and the rinsings titrated to determine the nitric acid (see below). The quantity of iron, if any, remaining unoxidized must be deducted from the quantity originally taken. It may be determined by weighing or (more conveniently) by measuring its length on a millimetre or other finely graduated scale."

Determination of the Nitric Acid. — "The temperature in the interior of the bomb during the combustion is so great as to bring about the combustion of some of the atmospheric nitrogen left in the bomb on filling, and also of some of the nitrogen contained in the substance burned. The product of this combustion is nitric acid. The heat produced by the combustion of the nitrogen is, of course, to be deducted from the total heat measured. For the determination of the nitric acid Stohmann advises the use of a solution of sodium carbonate containing 3.706 grams per litre. One cubic centimetre of this solution contains 0.003706 gram sodium carbonate, which is equivalent to 0.004406 gram nitric acid, the heat of formation of which is one calorie. Thus each cubic

centimetre of sodium carbonate used in the titration represents one calorie set free in the calorimeter by the combustion of nitrogen. Methyl orange is used as indicator."

DETERMINATION OF THE EQUIVALENT OF THE CALORIMETER.—"Now that the heats of combustion of many compounds are accurately known, the most convenient and satisfactory method for the determination of the water equivalent of a bomb calorimeter is to burn weighed quantities of such compounds in the bomb immersed in a known quantity of water. From the observed rise of temperature and the known heat of combustion of the compound used the total water value of the calorimeter system is calculated. Deducting from this the quantity of water used, we have the water value of the calorimeter itself.

"The substances used in these determinations should be such as can easily be obtained pure and preserved without risk of change by deliquescence, oxidation, decomposition, or otherwise. Their heats of combustion should have been determined in calorimeters whose water equivalents have been learned by other methods. Those which have been determined by several investigators, independently and with closely accordant results, are to be preferred."

"Camphor, hippuric acid, and benzoic acid are ignited directly by the heated iron wire, but with cane-sugar and glycocoll a kindler (a naphthalene crystal) should be used."

The following are the specific heats of combustion of the five substances in question:

Glycocoll	3131
Cane-sugar	3959
Hippuric acid	5664
Benzoic acid	6322
Camphor	9290

Calculation of Results.—The method of calculating the heat of combustion of a substance together with the mode

of tabulating the data is best explained by means of an example:

Capsule No. 1.
Wt. caps.+subs. = 4.2501
Wt. capsule = 2.8783
Wt. substance, W = 1.3718

CORRECTION FOR ACCESSORY COMBUSTIONS.
Wt. Fe 13.0 −1.1 = 11.9 mgs. = 19.0 cal.
Wt. naphthalene = 6.4 " = 61.6 "
HNO_3 = 6.6 "
Correction for accesories = 87.2 "

	READINGS.	CORRECTED READINGS.
INITIAL PERIOD.	1 1.018	1.015
	2 1.021	
	3 1.025	
	4 1.027	
	5 1.030	
	$6\theta_0$ 1.032	1.029
MAIN PERIOD.	$7\theta_1$ 2.300	2.3
	$8\theta_2$ 3.650	3.7
	$9\theta_3$ 3.678	3.7
	$10\theta_4$ 3.662	3.7
	$11\theta_5$ 3.653	.....

FINAL PERIOD.

$\frac{\theta_5+\theta_0}{2}$ = 2.3
Sum = 15.7
5ϑ = 5.1
Diff. = 10.6
Log. diff. = 0253
Log. $V'-V$ = 7324
Colog $\theta'-\theta$ = 5320
3397
Antilog. = + .0219
+5 V = − .014
Radiation correction = + .0079
16 3.640 | 3.633
Time 3.30

INITIAL PERIOD.
Fall = −.014
Rate V = −.0028
Mean $t°$, θ = 1.022

CORRECTED READING, θ_5 = 3.646
θ_0 = 1.029
$\theta_5+\theta_0$ = 4.675
$\frac{1}{2}$ = 2.3

FINAL PERIOD.
Fall = +.013
Rate V' = +.0026
V = −.0028
$V'-V$ = +.0054
Mean $t°$, θ' = 3.640
θ = 1.022
$\theta'-\theta$ = 2.618

THERMOMETER CORRECTION.
$T°$ air = 25.2
$t°$ water = 23.8
1st reading = 1.0
$T°$ of zero = 22.8
Corr. for 1° = +.001
Rise (degrees) = 2.6
Ther. corr. = +.0026

FINAL CALCULATION.
θ_5 = 3.646
θ_0 = 1.029
$\theta_5-\theta_0$ = 2.617
Th. corr. = +.0026
Rad. corr. = +.0079
Corr. rise = 2 6275
" "×2100 = 52.550
=Total heat = 5517.8
Accessories = 87.2
Corrected heat = 5340.6

Log. corr. heat = 734°5
Log. W 13729
59756

HEAT OF COMBUSTION PER GRAM = 3959

Heat of Formation.—The amount of heat liberated or absorbed in the formation of one gram-molecule of a substance is known as the *heat of formation.*

If the heat of combustion of the substance is known, this can be calculated according to the principle laid down by Hess. If the heat of combustion of a compound be subtracted from the sum of the heats of combustion of its elements, the remainder is the heat of formation. For example, the heat of formation of methane is determined by measuring the heat of combustion of the compound in oxygen and the heats of combustion of its elements in oxygen:

$$C,H_4 = C,O_2 + 2(H_2,O) - CH_4,O_4.$$
$$21,750 = 96,960 + 136,720 - 211,930.$$

The heat of formation of methane is thus 21,750 calories.

CHAPTER VIII.

THE SPECTROSCOPE.

THE apparatus used by the physical chemist for the approximate determination of wave-lengths and for spectrum analysis is the spectroscope of Bunsen and Kirchhoff. This apparatus is shown in Fig. 50. It consists of a col-

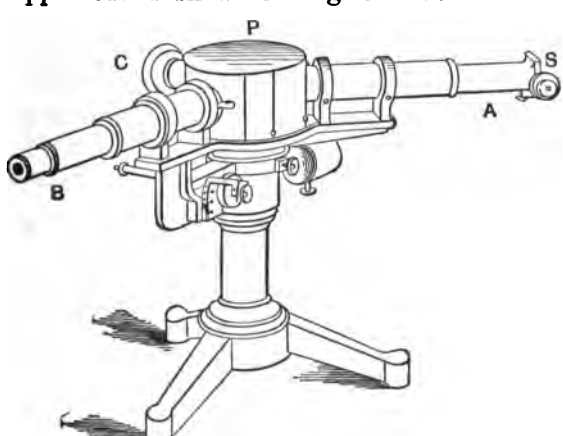

FIG. 50.

limator *A*, through which the light enters, the prism *P*, where the rays of light are dispersed, the observing-telescope *B*, and the sca'e-tube *C*.

The collimator is so adjusted that the rays which enter the slit S are rendered parallel before striking the prism P.

The width of the slit can be adjusted by means of a screw. The lower half of the slit is usually covered with a small comparison prism by means of which it is possible to compare two spectra directly without reference to a table of wavelengths.

The observing-telescope serves to form the image of the spectrum. The eyepiece is furnished with cross-wires which enable the observer to set the telescope upon a definite spectral line.

The image of the scale in the tube C is reflected from one face of the prism into the observing-telescope: this image is visible just above the image of the spectrum. The positions of definite lines of the spectrum can be determined by means of the relative positions of the lines and scale divisions.

Adjustment of the Spectroscope.*—(1) The slit must appear as a very distant object. After adjusting the eye-piece of the telescope so that the cross-wires appear sharp, the telescope is removed and focussed on some distant object, such as a tree or brick wall. When this has been accomplished the telescope is replaced, directed to the slit, and the latter drawn out until it appears clear and sharp.

(2) The prism must be adjusted to the position of minimum deviation. The slit is illuminated by the sodium flame and the prism placed approximately in the correct position before the lens of the collimator. When the direction of the refracted ray has been found with the naked eye, the image of the slit is sought with the telescope. The prism is then turned (following the image, if necessary, with the telescope) until the image stops and commences to move backwards. The prism is then fixed in this position.

* Kohlrausch, Physical Measurements.

(3) The reflected image of the scale should be clearly visible. It is illuminated by a gas-jet placed about 20 cm. from it. When by turning the tube the image is found, the length of the tube is adjusted until the image of the scale appears sharp. The images of the slit and scale should not change their relative positions on moving the eye before the eyepiece.

(4) The middle of the sodium lines should be made to coincide with the 100th division of the scale. This adjustment is made by turning the scale-tube until coincidence is attained; the tube should then be clamped.

Reduction of Scale-readings to Wave-lengths. — It is usual to express the positions of spectral lines in wave-lengths rather than in terms of an arbitrary scale.

In order to determine the wave-lengths which correspond to the various points of the scale, the positions of certain characteristic lines of known wave-length are carefully determined.

A series of salts giving lines throughout the whole visible spectrum are vaporized in a Bunsen burner before the slit. The following lines are chosen as being particularly well adapted to the purpose:

Elements.		Wave-lengths in Millionths of a Millimetre.
Potassium red	line K_α	768
" blue	" K_β	404.6
Lithium red	" Li_α	670.8
Sodium yellow	" Na	589.0–589.6
Thallium green	" Tl	534.9
Strontium blue	" Sr_β	460.8

The positions observed are plotted as abscissæ on coördinate-paper, while the corresponding wave-lengths are laid off as ordinates. The curve drawn through the points thus obtained enables the observer to express any scale reading in

terms of wave-lengths. It is obvious that this curve must be prepared with great care. The substances employed must be of a high degree of purity. The chlorides are usually employed, though sodium chloride is inconvenient on account of decrepitation, and hence the carbonate is used. The substances are introduced into the colorless Bunsen flame on a clean platinum wire, the glowing portion being placed so far down that no continuous spectrum appears. The slit should be narrow at first in order to separate any lines which may be close together, and then the observation should be repeated with a somewhat wider slit to insure the detection of fainter lines.

Should the intensity of the light diminish, it may frequently be restored by moistening the bead with hydrochloric acid, thus converting the oxide of the metal into the chloride. The platinum wire should be cleaned by moistening with hydrochloric acid, and then igniting before the blast-lamp until no color is imparted to the flame.

The flame will always be more or less colored with sodium, and the lower portion of the flame will give faint green and blue lines. Care must be taken to cut off extraneous light. The prism should be covered either with the cover furnished with the instrument or with a black cloth. A black-paper screen should also be placed around the eyepiece of the telescope to shield the eye from the illuminating flame. All of the optical measurements described should be made in a dark room the walls of which are painted with lampblack.

The scale should not be illuminated more strongly than is necessary to secure sharp readings, and in cases where the lines are very weak the light illuminating the scale should be extinguished.

Absorption Spectra.—Liquids and solutions give almost without exception broad absorption bands, the width of the

bands depending upon the concentration and the thickness of the layer of liquid.

The solution to be examined is placed in a glass cell with parallel sides between the flame and the slit. The best illuminant is the Welsbach light. To eliminate the influence of temperature on the absorption the solution should be kept within a few degrees of room temperature.

It is of importance to know not only the positions but also the intensities of the lines and bands of an absorption spectrum. The results are best recorded by photography,* but since this requires an outfit not often found in physico-chemical laboratories, the spectrum is sketched. The lines and bands are represented by black lines of equal length and varying width, or by a curve where abscissæ denote wave-lengths or scale divisions, and ordinates correspond to estimated intensities. The positions of maximum darkness in an absorption spectrum must be obtained with the greatest care.

Spectrophotometry.—By the term spectrophotometry is understood the measurement of the amount of absorption for a definite portion of the spectrum when the light is caused to pass through an absorbing medium. Of the many methods which have been devised for the measurement of absorption, that of Vierordt is best adapted to the needs of the physical-chemist. This method depends upon the use of a spectroscope the collimator of which is provided with a double slit. The intensity of the light is proportional to the width of the slit. If the slits be illuminated by two lights of different intensities, two spectra in contact, one above the other, will be observed: by adjusting one slit it will be possible to bring the two spectra to equal intensities,

* Ostwald, Zeit. phys. Chem., 9, p. 582, 1892.

when the ratio of the widths of the slits will be proportional to the intensities of the two lights. The absorption coefficient a is defined by the equation

$$i = i_0 e^{-ad},$$

where i is the intensity of the transmitted light, i_0 the intensity of the incident light, d the thickness of the absorbing layer, and e the base of the natural system of logarithms.

From this equation we see that

$$\log_e \frac{i}{i_0} = -ad,$$

or in Briggsian logarithms, making $\frac{a}{2.3} = A$, we have

$$A = -\frac{1}{d} \log \frac{i}{i_0}.$$

If, as is customary, d be made 1 cm., we have

$$A = -\log \frac{i}{i_0}.$$

The absorption coefficient A may be defined as the reciprocal of the thickness d, which makes $-\log \frac{i}{i_0} = 1$. That is, the equivalent of writing $i = \frac{1}{10} i_0$. The thickness then is that value of d which weakens the incident light one-tenth.

If the concentration of a solution is denoted by c, then when cd = constant we have equal absorption. If for a definite concentration the absorption coefficient A_0 has been found, and if for concentration c the absorption coefficient A has been determined, then

$$A = cA_0$$

and

$$c = \frac{A}{A_0}.$$

Thus it becomes possible to measure the concentration of a solution from the determination of the ratio $\frac{i}{i_0}$. The *specific absorption coefficient* is defined as the negative logarithm of the ratio $\frac{i}{i_0}$ when 1 gram of substance is dissolved in 1000 c.c. of solvent and observed with a Schulz glass (see below) 1 cm. thick.

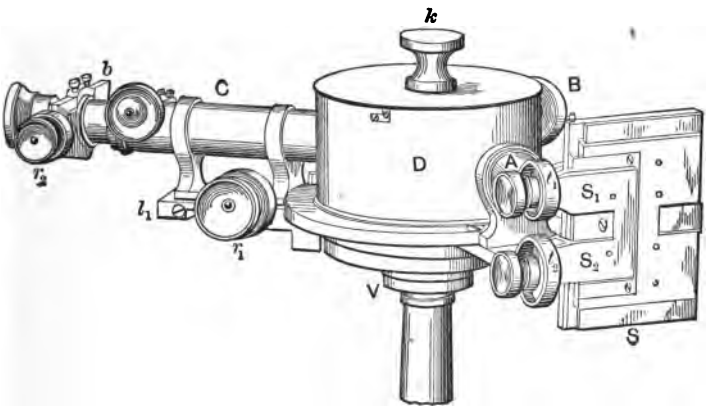

FIG. 51.

Apparatus.—The apparatus used is the universal spectrometer of H. Krüss (Fig. 51). This instrument is a modified form of the Bunsen apparatus. The essential points of difference are: (1) the various parts of the apparatus have been permanently adjusted by the maker; (2) the measuring device is especially accurate; (3) the instrument is furnished with an arrangement on the slit tube for quantitative measurements by the Vierordt method; and (4) there is also placed in front of the slits a Hüfner-Albrecht rhomb (Fig. 52) in such a position that its edge just falls at the edge of the slits. In addition to the spectrophotometer there is needed a Schulz glass and a Welsbach lamp. The

liquid to be examined is placed in a glass cell with parallel

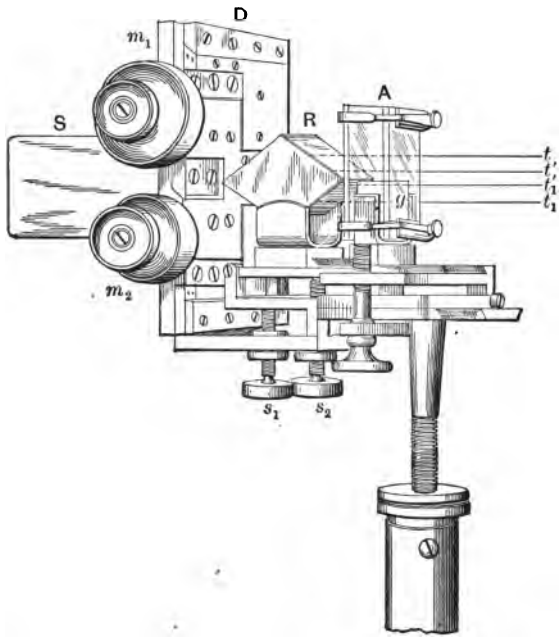

FIG. 52.

sides (Fig. 53) and 11 mm. in thickness. Within this vessel

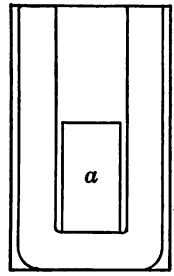

FIG. 53.

is placed the Schulz glass (*a*), a rectangular prism 10 mm. in thickness.

The light must thus pass through a layer of liquid either 1 mm. or 11 mm. in thickness.

The path of the rays through the absorption cell and the Hüfner-Albrecht rhomb is shown in Fig. 54. It is well to

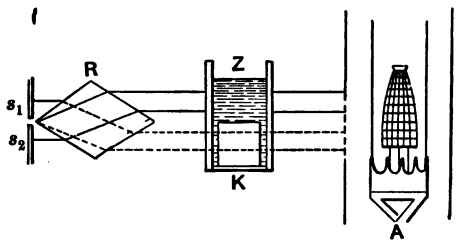

FIG. 54.

interpose a ground-glass plate between the burner and the cell, as shown in the sketch, so as to obtain a large, uniformly illuminated field.

Method of Operation.—The two halves of the slit must be equally illuminated by the Welsbach lamp. To establish this condition one slit is opened 30 divisions and the other adjusted so that the intensities in the green portion of the spectrum are the same. This adjustment must be repeated several times. If the lamp is properly adjusted, the second slit should be opened 30 divisions when the two spectra are of equal intensities. It is essential that the graduated screw-head should read 0 when the slit is closed. The vessel containing the liquid should be placed directly in front of the slit so that the upper surface of the Schulz glass is horizontal and in the same plane with the line bisecting the two halves of the slit. This adjustment is made by regulating the screws under the stand. The Hüfner-Albrecht rhomb must be adjusted by means of the proper screws so that its horizontal edge next to the slits is of the same height and in contact with the line bisecting the distance between the slits, and so

that its horizontal section lies in the optic axis of the collimator.

The scale attached to the telescope is used to ascertain the wave-lengths of the portion of the spectrum examined. That portion of the absorption spectrum should be used where there is no sudden change in intensity. The solution should not vary more than 5° from room temperature. Account must be taken of the influence of the solvent on the value of i. The following table taken from Krüss gives the adjustments of one micrometer-head for various solvents, the other micrometer being at 100:

Alcohol, 90%.	95.0
Alcohol (absolute).	110.0
Ether (aqueous).	98.0
Ether (anhydrous).	91.5
Chloroform (anhydrous).	112.0
Benzene (anhydrous).	102.5
Glacial acetic acid (anhydrous).	88.0

For accurate work it is well not to rely upon this table, but to determine the value for the solvent in use. The concentration of the solution should be so chosen that adjustment to equal intensity requires the narrowing of the width of the slit from division 100 to division 20.

For further details concerning spectrophotometry the student is referred to Kolorimetrie und quantitative Spectralanalyse von G. und H. Krüss, Hamburg and Leipzig, 1892.

REFRACTIVE INDICES.

The Pulfrich Refractometer.—*Apparatus.*—This instrument is shown in Fig. 55. It consists of a right-angled prism, the horizontal and vertical faces of which form the right angle. This prism is made of highly refracting glass, and is mounted upon the top of a hollow triangular support,

which in turn rests upon the base of the instrument. Upon the upper surface of the prism, which is slightly curved, is cemented a small glass cylinder provided with a thermometer.

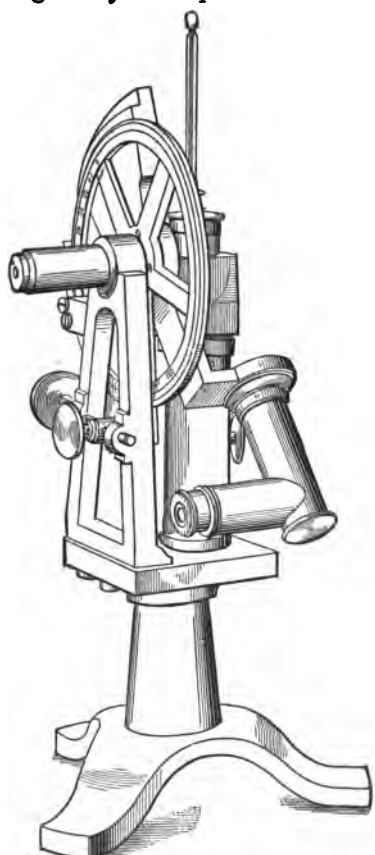

FIG. 55.

Into this cylinder the liquid to be examined is placed. By means of a lens the rays of light are brought to a focus at the base of the small cylinder filled with liquid. The rays will pass from the liquid into the prism, and will emerge from

the vertical face provided the angle formed with the normal to the surface is smaller than the angle of total reflection. By means of a telescope placed opposite the vertical surface of the prism the position of the emergent ray may be found. The telescope is provided with a graduated circle which rotates with it, and the eyepiece is furnished with cross-wires. There is also a vernier and reading-microscope by

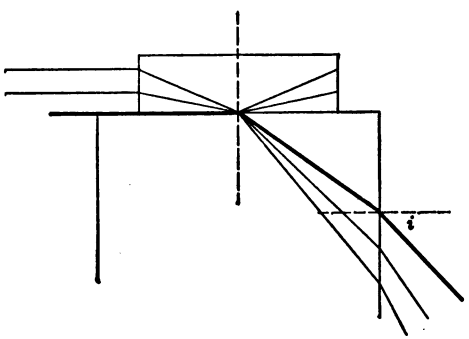

FIG. 56.

means of which the angle of rotation of the telescope may be read to minutes of arc.

The position of the telescope is determined for which the cross-wires intersect upon the line dividing the field of view into light and dark.

By substituting in a formula the angle through which the telescope has been rotated from the zero of the scale to the required position, the index of refraction of the liquid can be calculated.

Principle.—In Fig. 56 is shown the path of the rays through the liquid and the prism.

If N denotes the index of refraction of the prism, n the index of refraction of the liquid, e the angle of refraction, and

i the angle of emergence, then we have

$$\frac{N}{n}=\frac{1}{\sin e};$$

but

$$N=\frac{\sin i}{\sin (90°-e)}$$
$$=\frac{\sin i}{\cos e}$$
$$=\frac{\sin i}{\sqrt{1-\frac{n^2}{N^2}}};$$

hence

$$N^2-n^2=\sin^2 i,$$

and

$$n=\sqrt{N^2-\sin^2 i}.$$

The value of n must be less than N.

It is obvious that the values of both n and N are dependent upon the wave-length of the light used. Sodium light is usually employed. The values of N for sodium, lithium, and thallium flames are:

	N
Na	1.61511
Li	1.60949
Tl	1.62043

Before using the refractometer it should be tested with pure water or some other pure liquid of which the refractive index is accurately known. For water the value of n at 15° is 1.3336, and at 20° 1.3332. Where many measurements are to be made with the refractometer a table giving the different values of n for corresponding values of i for sodium light is a great convenience. The results are generally

given for angles differing by 10′, the intermediate values being obtained by interpolation.

Method of Operation. — The source of light is placed about fifty centimeters from the apparatus, and by means of a sheet of white paper held in front of the cylinder the position of the light is adjusted until a sharp, inverted image of the flame is obtained. This image should be a little above the upper face of the prism, toward the middle of the cylinder.

The liquid to be examined is then introduced into the cylinder by means of a pipette. The telescope is then turned from the normal position until the light and dark field is observed. The telescope is then clamped, and by means of the tangent-screw the intersecting cross-wires are brought upon the line of division between the light and dark fields. The angle, i, through which the telescope has been turned is then read off to minutes of arc. Care must be taken to keep the temperature constant throughout a series of determinations, since the refractive index changes with the temperature. Successive readings should not differ more than one minute: this will insure the accuracy of the determined refractive index to within one unit in the fourth decimal place.

Care must be taken in using the instrument that the glass cylinder does not become detached. Should this happen, the cylinder may be replaced by a cement of balsam or gum arabic.

In re-cementing the cylinder great care must be taken that, at the place where the light enters, the edge of the upper plane surface should be free from cement, since sharp definition can only be secured under this condition.

The Abbe Refractometer.—*Apparatus.*—This instrument is shown in Fig. 57. By means of the concave mirror g light

is reflected into the specially constructed combination prism C; the rays after emergence from the prism pass through the

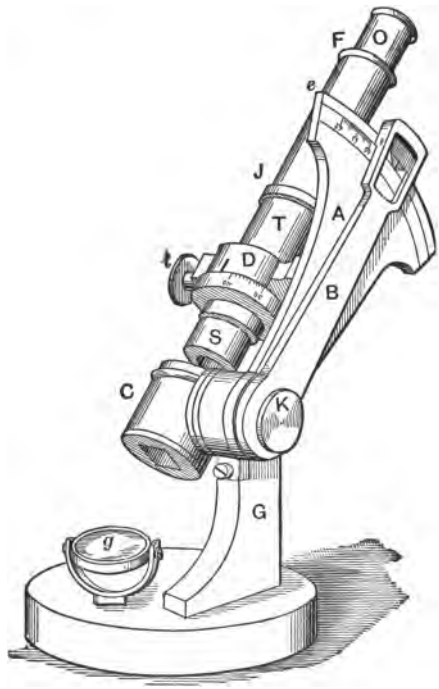

FIG. 57.

compensator D and the telescope JO, the eyepiece of which is provided with cross-wires. The telescope is attached to the divided arc A and the prism C with the arm B, so that the relative positions of telescope and prism can be altered. By means of the screw-head K the telescope can be fastened in any position desired. The liquid to be examined is placed between the prisms in C; for a certain position of the prism the light will be totally reflected at the surface of the liquid and glass, and the field of view in the telescope will be

darkened. For a definite position of the prism one half of the field will appear dark and the other half light.

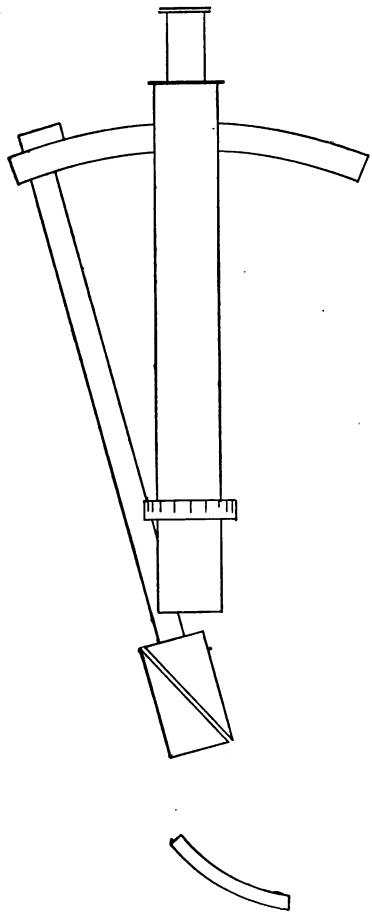

FIG. 58.

The sector A is so graduated that the index of refraction of the liquid for sodium light can be read directly. If it is desired to use white light, the compensator D must be em-

ployed, since the several colors of the spectrum do not suffer total reflection simultaneously. The compensator consists of a system of direct-vision prisms, the two parts of which can be turned in opposite directions by means of the screw *t*. The compensator is so adjusted that the rays of sodium light are not diverted. By means of the scale *C* the positions of the screw *t* for which the effect of dispersion is eliminated are determined. A schematic drawing of the instrument (Fig. 58) shows clearly the arrangement of the prism combination. The apparatus is based upon total reflection taking place at the thin film of liquid inclosed between the two prisms. The prisms must necessarily have a higher index of refraction than the interposed liquid film.

Method of Operation.—By means of the screw-head *K* the sector *e* is turned until the lower edge is in contact with the table. The movable prism is then carefully taken out by pressing the spring which holds it in place (Fig. 59);

FIG. 59.

the faces of the prism are then washed with alcohol and ether. A piece of thin paper is first placed on the short side of the prism and then a drop of the liquid to be examined is brought upon the long face of the permanently fixed prism. The movable prism is then replaced and the telescope turned until *B* stands at the first division of the graduated arc.

The mirror g is then turned toward the source of light (Welsbach burner) and adjusted until the field of view is wholly bright. The arm B is then turned until the lower part of the field becomes dark. The dividing line between the dark and bright fields will usually be colored and not sharp.

Now the screw t is turned until the dividing line between the two fields is sharp, and then by turning the arm B the intersection of the cross-wires is brought upon the line of division. The readings of the arm and compensator are then noted. The screw t is again turned until the line of division appears sharp and free from color, when the readings are again noted. The average of these readings on the arm gives the refractive index for the sodium line. The results are accurate to one or two units in the fourth place of decimals.

The accuracy of the instrument should be tested by determining the indices of refraction of several pure liquids of which the refractive indices are accurately known. Owing to the small amount of liquid used errors due to variation of temperature are more liable with the Abbe than with the Pulfrich apparatus.

The Abbe refractometer may be used to determine the refractive index of solids.

The solid is made into a thin polished plate which together with a drop of some indifferent and highly refracting liquid is placed between the prisms. The index of refraction of the plate and liquid being denoted by n' and the index of refraction of the indifferent liquid compared with air by n, then the index of refraction of the solid $N=\frac{n}{n'}$.

Among indifferent liquids which may be used are the following:

	n
Oil of cassia	1.60
Cinnamic aldehyde	1.62
Sulphur chloride	1.654
Selenium chloride	1.653
Phenyl sulphide	1.623
Phosphorus bromide	1.68
Arsenic bromide	1.781
Monobrom-naphthalene	1.66

For other refractive indices see Landolt and Börnstein's Tables.

Refraction Constants.—Of several formulas which have been proposed to express the relation between chemical composition and refractive indices only two need be mentioned. These formulas are:

(Gladstone and Dale Formula) $$R_1=\frac{n-1}{d}, \quad \ldots \quad (1)$$

(Lorenz-Lorentz Formula) $$R_2=\frac{1}{d}\cdot\frac{n^2-1}{n^2+2}, \quad \ldots \quad (2)$$

where n is the index of refraction and d is the density determined at the same temperature as n.

Formula (2) is most used, since it finds support both theoretically and experimentally.

If in the above formulas either the atomic or molecular volume is introduced in place of the factor $\frac{1}{d}$, the resulting constants are known as the atomic or molecular refractions respectively. For mixtures the following equations are found to hold approximately:

$$(n_1-1)v_1+(n_2+1)v_2+\ldots=(N-1)V,$$

and

$$\frac{n_1^2-1}{n_1^2+2}v_1+\frac{n_2^2-1}{n_2^2+2}v_2+\ldots=\frac{N^2-1}{N^2+2}V,$$

where $v_1, v_2 \ldots$ and $n_1, n_2 \ldots$ are the volumes and refractive indices of the components, and N and V the corresponding values for the mixture.

Refractive indices may be used to determine the concentration of a solution. For this application of the refractivity see Schütt, Zeit. phys. Chem., **5**, 349, and **9**, 349.

The determination of the refractive index may also serve to throw light on the constitution of a chemical compound. The discussion of this subject is out of place here, but the student is referred to the work of Brühl and others in this field.*

The Polarimeter.—The polarimeter is an instrument for measuring the rotation of the plane of polarization. It is well known that many solids, liquids, and gases have the power to rotate the plane of polarization. If monochromatic light be transmitted through a Nicol prism, its vibrations are reduced to a single plane, or it is said to be polarized. If the polarized beam be examined by means of a second similar Nicol prism, there will be found two positions 180° apart at which the ray will be transmitted unobstructed, while in positions midway between these two, viz., at 90° and 270°, the polarized ray will be completely cut off. These two prisms are known as the *polarizer* and the *analyzer*.

If, when the polarizer and analyzer are so adjusted with reference to each other that no light can pass, a tube containing some optically active liquid is interposed, the system will then transmit the incident light. By turning either the analyzer or the polarizer a position will be found in which the field again becomes dark. The object of all polarimeters is

* Brühl, Ber. d. d. chem. Ges., **12**, 2135; **19**, 3103. Brühl, Liebig's Ann., **200**, 139. Brühl, Zeit. phys. Chem., **1**, 311; **7**, 1. Wallach, Liebig's Ann., **245**, 191. Kanonnikoff, Jour. prakt. Chem., **32**, 497.

to measure the angular rotation necessary to restore maximum darkness.

The simplest conceivable polarimeter would consist of a polarizer, polarization-tube, and analyzer fitted with a graduated circle. Such a polarimeter was first made by Biot and later improved by Mitscherlich, but since the mean error of the readings is nearly $\pm 0°.1$, it finds little use in the physico-chemical laboratory. Much ingenuity has been displayed in improving the polarimeter and increasing its sensitiveness, and as a result many different forms of apparatus are to be found. The introduction of the so-called *half-shadow* principle has increased the sensitiveness of the polarimeter to a marked degree. The two forms of apparatus best suited to the needs of the physical chemists are the polarimeters of Laurent and Lippich, both of which are half-shadow instruments.

The Laurent Polarimeter.—The arrangement of parts in this apparatus is shown in Fig. 60. Sodium light enters the

FIG. 60.

polarimeter after having traversed a plate of potassium dichromate crystal, which acts as a ray-filter, thus insuring monochromatic light. The rays then enter the polarizer *d*, after leaving the lens *e*, which renders them parallel. Upon emergence from the polarizer they enter a diaphragm, *f*, one-half of which is covered with a quartz plate which is cut parallel to the axis, and is of such thickness that the rays of sodium light are changed in phase by one-half a wave-length. From the diaphragm the rays pass through the polarization-tube *p*, then through the analyzer *g*, and finally through the

eyepiece. If the polarizer is so adjusted that the plane of vibration of the light is parallel to the axis of the quartz plate, then, whatever the position of the analyzer, the field of view will consist of two equally bright halves. If, however, the polarizer forms an angle α with the axis of the quartz plate, the plane of polarization of the rays which pass through the quartz will be displaced in the opposite direction. Under these circumstances the field of view appears divided into two halves, as shown in Fig. 61, which for all positions of the Nicol except two, 180° apart, are unequally illuminated.

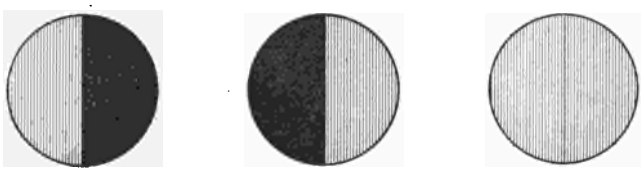

FIG. 61.

The zero of the instrument is this position of uniform illumination of field. To the eyepiece and analyzer is attached an arm carrying a vernier which moves over a fixed graduated circle.

The vernier can be read by means of a small reading-microscope. The axis of the quartz plate and the plane of the polarizer are adjusted to the desired angle by means of an arm attached to the polarizer.

The smaller the angle between the axis of the quartz plate and the plane of the polarizer the more sensitive the instrument becomes. The polarizer should be adjusted to that position for which there is the maximum change in shade in the field for a very small rotation of the analyzer.

The zero-point should be determined with the tube filled with pure water in order that the intensity of the field may

be comparable with that when the optically active substance is introduced.

The intensity of the field may be increased by a slight rotation of the analyzer, but it must be remembered that increase in illumination is gained at the expense of sensitiveness.

The mean of the measurements 180° apart should be taken as the true value for the rotation.

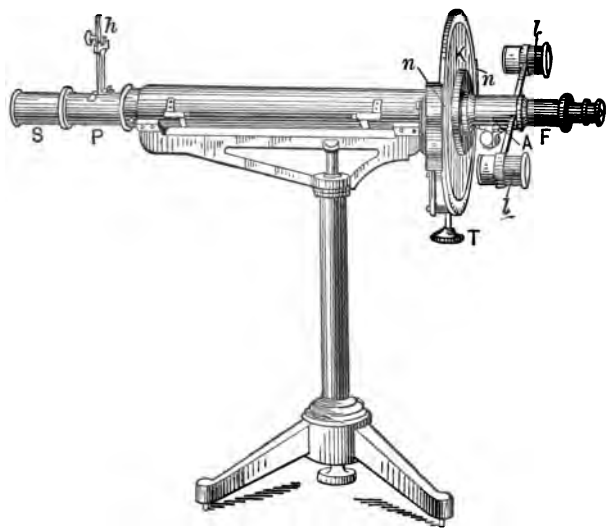

FIG. 62.

The mean error for the settings with the Laurent apparatus may be taken as ± 2 minutes of arc. A very serious objection to the apparatus of Laurent is that it can be used with light of only one wave-length. This difficulty is overcome in the instrument of Lippich.

The Lippich Polarimeter.—This instrument is shown in Fig. 62, and the arrangement of the optical system is shown in Fig. 63.

The construction is very simple, and at the same time it affords the best polarizing apparatus known.

Just beyond the polarizer N_1 there is placed a small Nicol prism, N_2, which is so adjusted that one edge lies in the axis of the apparatus and bisects the circular polarizer diaphragm D. The small prism N_2, which is called the "half-prism," is fixed, while the polarizer N_1 is movable about the axis of the tube, thus making it possible to change the half-shadow. The principal sections of the prisms N_1 and N_2 may form with each other a small angle α, so that the light coming from the polarizer and passing through the free half

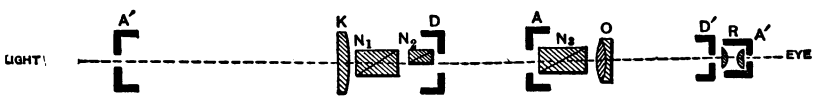

FIG. 63.

of the field of view is polarized vertically to the principal section of N_1, whereas the other portion of the light is broken up into two components on entering N_2, of which only the rays vertical to the principal section of the half-prism emerge. Hence the light which comes through the covered half of the field of view is polarized vertically to the principal section of the prism N_2, and the whole field is composed of two halves whose planes of polarization form with each other the small angle α. The light of each half remains linear for all wave-lengths, and polarized in the same direction. There is a slight difference in the intensities of the two halves of the field of view, owing to the absorption of light in transmission through the half-prism. In the inital or zero position, therefore, the principal section of the analyzer N_3 cannot bisect the angle of half-shadow.

In using the Lippich polarimeter the angle α should be made as small as possible. With a light of medium bright-

ness and a half-shadow angle of 1° the mean error of reading is about ±15 seconds of arc.

Lamp for Homogeneous Light.—The most convenient lamp consists of an elongated Bunsen burner mounted upon a heavy foot and furnished with a chimney of sheet iron. In one side of the chimney is an opening through which the flame can be observed. Upon the top of a short vertical support which can be rotated there is fastened a horizontal arm which carries upon its end a small annular trough of platinum. This trough may be filled with sodium carbonate, and by turning the support it can be introduced into the flame. Such a lamp will furnish an intense yellow light for some time without renewal of the sodium carbonate.

Observing-tubes.—The ordinary form of observing-tube consists of a thick-walled glass tube the ends of which are ground to planes accurately perpendicular to the axis of the tube. To the ends of the tube are cemented brass tubes upon which deep threads are cut. Upon these brass tubes are screwed caps of brass which press plane glass plates firmly against the ends of the observing-tube. In order to insure the tubes against leaking, and also in order to avoid the application of too great pressure, the caps are provided with rubber rings.

Since changes in temperature cause marked changes in the optical activity of almost all substances, it is almost indispensable to have some device by which the temperature of the liquid within the tube may be kept constant. By surrounding the tube with a jacket similar to the Liebig's condenser it is possible to circulate water of a constant known temperature and thus secure constant temperature within the tube. Since the exclusion of the last air-bubble in filling an observing-tube is frequently a source of much

vexation, the form of tube shown in Fig. 64 is to be recommended.

Before using a tube it must be thoroughly cleaned. This is accomplished by removing both caps and running pure water through the tube, after which it is dried by pushing through it rolls of soft linen cloth with a wooden stick. The glass plates are then carefully washed and dried, and one is placed over one end of the tube and fastened down by means

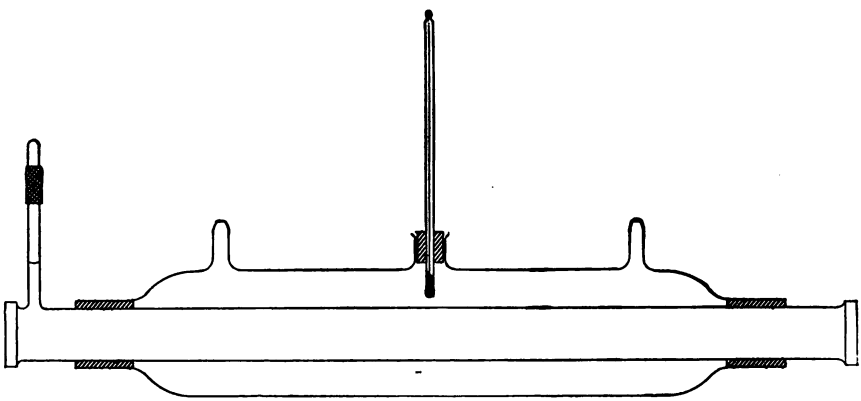

FIG. 64.

of the screw-cap. Care must be taken in fastening the plates, since if too great pressure is applied they become doubly refracting and thus introduce errors in the subsequent measurements. The tube is then filled with the liquid under investigation until a flat meniscus appears above the upper end of the tube. The second plate is then slipped over the end of the tube and fastened in place, care being taken to avoid the entrance of an air-bubble. The tube is then placed in position, and when it has acquired the desired temperature the readings are taken. In all measurements with the polarimeter an initial reading must be taken with the tube filled with pure distilled water. The polarimeter is

ordinarily furnished with several tubes of varying length, the lengths being indicated on the tubes.

Specific Rotation.—The specific rotation of an optically active liquid is the rotation produced by a column of liquid 10 cm. in length. If the liquid is a solution, it is the rotation produced by a column of the solution 10 cm. in length, the solution containing 1 gr. of substance in 1 c.c. of volume.

Denoting the density of the solution by d, the length of the column in decimetres by l, and the rotation produced by α, then the specific rotation A for light of a definite wave-length is

$$A = \frac{\alpha}{dl}.$$

Molecular Rotation.—The molecular rotation is the rotation produced by one gram-molecule of the substance, or

$$M = \frac{m\alpha}{100dl} = \frac{mA}{100}.$$

The arbitrary factor 100 is introduced to avoid large numbers.

For a solution containing C grams of substance in 100 c.c. of solvent the specific rotatory power for the concentration given is calculated from the formula

$$A = \frac{100\alpha}{lc},$$

or

$$M = \frac{m\alpha}{lc}.$$

On the other hand, if g grams of substance are contained in 100 gr. of solution of density d, then the specific rotatory power is

$$A = \frac{100\alpha}{lgd},$$

or

$$M = \frac{m\alpha}{lgd}.$$

Rotation Dispersion.—The degree of rotation produced by an active liquid is dependent upon the wave-length of the light employed. The rotation is greatest for the violet and least for the red, the amount of rotation therefore increasing with decrease in wave-length. Biot first proposed a formula connecting the amount of rotation with wave-length, but this was later found to be only an approximation.

The two formulas which are accepted to-day as nearly correct are those of Boltzmann and Lommel, which are respectively

$$\alpha = \frac{A}{\lambda^2} + \frac{B}{\lambda^2}$$

(where A and B are constants) and

$$\alpha = \frac{a}{\lambda^2\left(1 - \frac{\lambda_0^2}{\lambda^2}\right)^2}.$$

(where a and λ_0 are constants).

The values of these constants are determined by measuring the rotations α_1, α_2, α_3, etc., produced by light-waves of known lengths λ_1, λ_2, λ_3, etc., and then solving the equations for the constants.

It is obvious that these two formulas may also be used

to determine the wave-length of light by solving them for λ. The polarimeter is also of service to the physical-chemist in the study of certain problems in chemical dynamics, such as the rate of inversion of cane-sugar. Its use in this connection will be explained in a later chapter. The student who would become familiar with the various forms of polarizing apparatus and their uses is referred to "Das optische Drehungsvermögen" by Landolt (English translation, "The Optical Rotation of Organic Substances," by Long).

CHAPTER IX.

ELECTRICAL UNITS.

ELECTRICAL energy, as well as every other form of energy, may be resolved into two factors—a *capacity* factor and an *intensity* factor, or the electrical energy

$$E = \epsilon\pi,$$

where ϵ is the capacity factor and π the intensity factor. The capacity factor of electrical energy is the *coulomb*, while the intensity factor is the *volt*.

All electrical measurements ultimately resolve themselves into the determination of these two factors, although we frequently arrive at the result through the measurement of certain derived quantities which bear to them well-known relations. Of these relations the following may be taken as typical:

$$I = \frac{E}{R}, \quad \ldots\ldots\ldots \quad (1)$$

where I is the current strength, E the potential, and R the resistance;

$$I = \frac{Q}{T}, \quad \ldots\ldots\ldots \quad (2)$$

where I has the same significance as above and where Q denotes the quantity of electricity which flows in the time T.

From relations (1) and (2) we may derive the following:

$$R=\frac{E}{I},\quad \frac{1}{R}=\text{conductivity}=\frac{I}{E}=\frac{Q}{E\times T}.$$

Since the galvanometer and the resistance-box enable us to measure current strengths and resistances with comparative ease, these derived magnitudes assume great practical importance.

The following definitions of practical electrical units are taken from the Proceedings of the International Electrical Congress held in Chicago, August 21, 1893:

"*Resolved*, That the several governments represented by the delegates of this International Congress of Electricians be, and they are hereby, recommended to formally adopt as legal units of electrical measure the following:

"1. As a unit of resistance, the *international ohm*, which is based upon the ohm equal to 10^9 units of resistance of the C.G.S. system of electromagnetic units, and is represented by the resistance offered to an unvarying electric current by a column of mercury at the temperature of melting ice, 14.4521 grams in mass, of a constant cross-sectional area and of the length of 106.3 centimetres.

"2. As a unit of current, the *international ampere*, which is one-tenth of the unit of current of the C.G.S. system of electromagnetic units, and which is represented sufficiently well for practical use by the unvarying current which, when passed through a solution of nitrate of silver in water, in accordance with accompanying specification, deposits silver at the rate of 0.001118 gram per second.

"3. As a unit of electromotive force, the *international volt*, which is the E.M.F. that steadily applied to a conductor

whose resistance is one international ohm will produce a current of one international ampere, and which is represented sufficiently well for practical use by $\frac{1000}{1434}$ of the E.M.F. between the poles or electrodes of the voltaic cell known as Clark's cell.

"4. As the unit of quantity, the *international coulomb*, which is the quantity of electricity transferred by a current of one international ampere in one second. . . .

"6. As the unit of energy, the *joule*, which is 10^7 units of work in the C.G.S. system and which is represented sufficiently well for practical use by the energy expended in one second by an international ampere in an international ohm."

These units were made legal by Act of Congress on July 12, 1894.

Sources of Current.—By far the best source of current for the physico-chemical laboratory is the storage-cell. Of the several forms of storage-cells which are on the market all are based upon the same principle. The electrodes consist of two lead plates or grids the interstices of which are filled with a paste of lead sulphate made by mixing one of the oxides of lead with dilute sulphuric acid. These electrodes are immersed in dilute sulphuric acid and a current is sent through the cell. The chemical changes within the cell are very complex, but the chief action of the current consists in the liberation of hydrogen at one electrode which reacts with the lead sulphate, forming spongy lead and sulphuric acid, which dissolves; the SO_4 ions upon reaching the other electrode react as follows:

$$PbSO_4 + SO_4 + 2H_2O = PbO_2 + 2H_2SO_4.$$

The sulphuric acid formed dissolves, while the lead dioxide remains on the grid. When the greater part of the lead sulphate has been converted into metallic lead and lead diox-

ide the cell is "charged," and may be used as a source of current. The current flows in the opposite direction to the charging current until the battery is discharged, when the charging process is repeated. The storage cell is remarkable for its efficiency, nearly 80 per cent. of the energy supplied in charging being recovered on discharging.

The voltage of a freshly charged accumulator is nearly 2.5 volts, which gradually falls to about 1.8 volts as the discharge continues. The quantity of electricity which a storage-cell can furnish is approximately 0.04 ampere-hour for each square centimetre of surface of lead dioxide exposed. An accumulator should never be charged or discharged more rapidly than 0.01 ampere per square centimetre of electrode surface. The discharge should never be continued below 1.7 amperes. The specific gravity of the acid solution should be 1.18; this will fall to about 1.15 after discharge. In charging the battery the positive pole is connected with the positive pole of the dynamo, and the negative pole with the negative pole of the dynamo, a variable resistance being introduced so that the strength of the charging current may be altered at will. The charging is continued until there is a vigorous evolution of gas.

The lead-sulphate paste in the grids suffers considerable expansion and contraction during charge and discharge, for which reason it is essential always to charge the battery in the same direction.

The grids suffer disintegration after a time, so that it is necessary to renew them.

For currents of lower voltages the well-known primary cells of Daniell and Le Clanché are of service.

The Daniell cell, which is designed for closed-circuit work, furnishes ordinarily an E.M.F. of 1.08 volts, and remains constant for quite a period of time.

The Le Clanché cell is intended for use on open circuit; the initial E.M.F. of the cell varies from 1.4 to 1.7 volts, and the internal resistance from about 0.4 to 2.0 ohms. Cells which serve as standards of electromotive force will be considered in another place.

CHAPTER X.

RESISTANCE (CONDUCTIVITY).

THE three electrical quantities which the physical chemist has most frequently to measure are resistance or its reciprocal, conductivity, current strength, and electromotive force. In other words, the three quantities involved in the equation

$$I = \frac{E}{R}.$$

Conductors of electricity are usually divided into two classes, though there is much doubt as to whether there is any true distinction between them: (1) those which conduct the current without suffering chemical decomposition, and (2) those which undergo chemical change when traversed by the electric current. To the first class belong the metals and carbon, while to the second belong the solutions of many substances which undergo decomposition at the poles. It is with the second class of conductors that we are chiefly concerned.

These conductors are known as electrolytes, and include chiefly the solutions of acids, bases, and salts. There are many substances which in solution do not conduct the electric current, and these are known as non-electrolytes; among these may be mentioned the alcohols, the ketones, and the hydrocarbons.

Specific and Molecular Conductivity.—The *specific resistance* of a conductor is the electrical resistance of a centimetre cube of it when the current flows through it from one face to the face opposite. Specific resistance is wholly dependent upon the nature of the conductor. Denoting the specific resistance by s', and the length and cross-sectional area of the conductor by l and a respectively, then the resistance is

$$r = \frac{s'l}{a},$$

or

$$s' = \frac{ra}{l}.$$

Since conductivity is the reciprocal of resistance, it follows that the specific conductivity of the conductor is

$$s = \frac{l}{ra}.$$

Conductors of the second class, as has been said, consist of solutions of an electrolyte in some solvent, and since liquids have no definite form it is obvious that the above definition of specific conductivity does not apply. Since the conductivity of solutions depends upon the dissolved electrolyte, we select the gram-molecular weight of dissolved substance in a litre as the basis of a definition which shall render the resistances of all solutions comparable. Consider a litre of solution containing a gram-molecular weight placed between two electrodes which are separated by a distance of 1 cm. The cross-section will be 1000 cm.^{2} This will have $\frac{1}{1000}$ the resistance or 1000 times the conductivity of a centimetre cube of the same solution.

If v denotes the number of cubic centimetres of any solution containing a gram-molecule of dissolved substance,

and s represents the specific conductivity of a centimetre cube of the solution, the molecular conductivity μ is

$$\mu = v \times s. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Where g gram-molecules of dissolved substance are contained in a litre of solution, we have as a perfectly general expression

$$\mu = s\frac{10^3}{g}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

If the specific conductivity be referred to a cylinder of solution 100 cms. in length and 0.1 cm. in cross-section, then obviously (1) and (2) become

$$\mu = 10{,}000vs, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$\mu = s\frac{10^7}{g}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Thus when solutions of the same concentration are employed their molecular conductivities are directly comparable.

Resistance-boxes.—In the measurement of the resistance of electrolytes, as in the measurement of other resistances, it is necessary to have a series of known resistances the values of which have been determined with great accuracy. Such a series of resistances is to be had in the ordinary resistance-box (Fig. 65). This consists of a series of coils of insulated wire wound double upon spools in order to avoid self-induction on starting or stopping the current. Each coil is exactly adjusted to give the desired resistance and then is fastened to the under side of the hard-rubber cover of the box. Its ends are soldered to two heavy copper rods which pass through the cover and are connected to the heavy brass blocks upon the top of the cover of the box. The several coils are con-

nected in series by the insertion of accurately fitting brass plugs in the holes between the segments of brass upon the cover. Thus when any plug is withdrawn the current must traverse the coil which bridges the gap between the disconnected brass blocks. Opposite each hole upon the cover is marked the resistance of the underlying coil. The coils are usually adjusted to the following resistances in ohms: 1, 2, 2, 5, 10, 10, 20, 50, 100, 100, 200, 500, 1000, 2000, 2000, 5000, making a total of 11,000 ohms in the box. Each box is

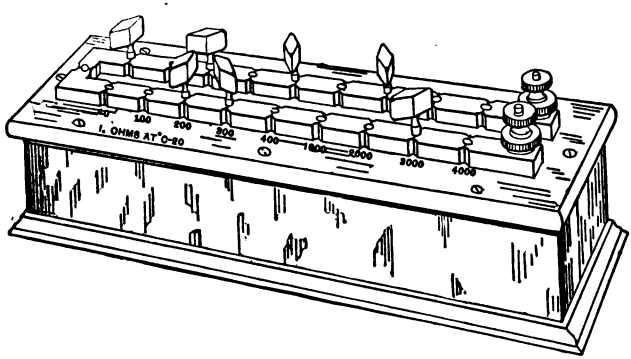

FIG. 65.

adjusted to some convenient temperature, which is marked upon the cover of the box. Should the room temperature vary from that for which the box is adjusted, corrections may be introduced provided the temperature coefficient of the wire from which the coils are wound is known. For manganin wire the temperature coefficient ranges from +0.00001 to +0.00004.

The plugs of a box should fit very exactly in their conical sockets, and care should be taken to insure the plugs being clean and free from oxide. This is accomplished by rubbing them with a cloth dipped in a *very weak* solution of oxalic acid; grease may be removed by washing them with alcohol and ether.

In inserting the plugs too great pressure should not be applied, otherwise there is danger of breaking the rubber tops upon removal. The actual resistance through a plug when it is well cleaned and firmly seated is from 0.00005 to 0.0001 ohm.

A good resistance-box should be protected when not in use by a light wooden box.

When in use care should be taken that direct sunlight does not fall on the box, neither should it be used in a room where corrosive fumes are liable to be liberated.

Wheatstone's Bridge.—For the measurement of all but very high or very low resistances the Wheatstone's bridge

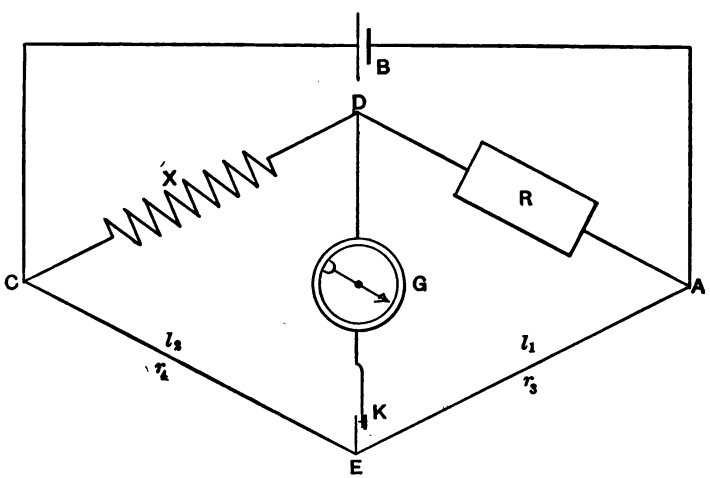

FIG. 66.

is the most convenient. It consists of a combination of resistances, as shown in Fig. 66. It is obvious that in the divided circuit from *C* to *A* there must be a point on the branch *CDA* which will have the same potential as a point on the branch *CEA*. Let us imagine that by means of the galvanometer *G* two such points have been found, and let

these points be denoted by D and E. Then we have the following proportion:

$$R : X = r_3 : r_4,$$

or

$$Rr_4 = Xr_3.$$

From this equation it is evident that if the values of any three of the four resistances are known the other one is determined.

Let us imagine the resistance-box to be inserted in the arm R and the unknown resistance to be placed in the arm X; then we can alter the position of the point E until the galvanometer shows no deflection, and thus determine the lengths of CE and AE. Since resistance is directly proportional to the length of the conductor, it follows that the values of r_3 and r_4 are proportional to the lengths $AE = l_1$ and $CE = l_2$, or

$$x = \frac{l_2 R}{l_1}.$$

The most convenient form of the Wheatstone's bridge is the slide-wire-metre bridge, Fig. 67. In this form of bridge

FIG. 67.

(Fig. 68) the conductor AEC, corresponding to the similarly lettered portion of Fig. 66, is made of a thin uniform wire one metre long, the point E being determined by a sliding contact which moves over a millimetre scale. The arms CD and DA of the bridge consist of heavy copper straps which offer inappreciable resistance. The lettering in the two diagrams being the same, the latter becomes self-explanatory. A single determination of the position of the index is not

reliable owing to variations in the size of the wire and to lack of precision in determining the point of balance. For these reasons the mean of a series of observations should be taken.

When a direct current is passed through the solution of an electrolyte bubbles of gas appear on the electrodes after a very short time, or, as we say, polarization sets in. Polarization causes a counter E.M.F., which makes the accurate measurement of conductivity an impossibility. This

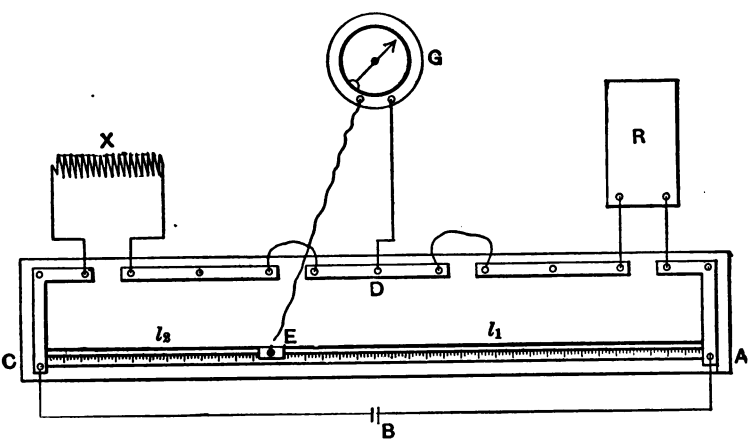

FIG. 68.

difficulty has been overcome by Kohlrausch, who introduced the use of the alternating current. The alternating current is furnished by a small inductorium, the wires from the secondary of which are connected with the ends of the bridge-wire. Since the galvanometer cannot be used with the alternating current, it is replaced by a telephone. The inductorium is best placed in another room from that in which the bridge is placed, so that the sound of the coil can only be heard through the telephone. The sliding contact is then moved along the bridge-wire until a point is found

where the sound of the coil either entirely vanishes or attains a minimum of intensity. This point is the position of balance between the arms of the bridge. A very convenient form of telephone is that shown in Fig. 69, where the ear-

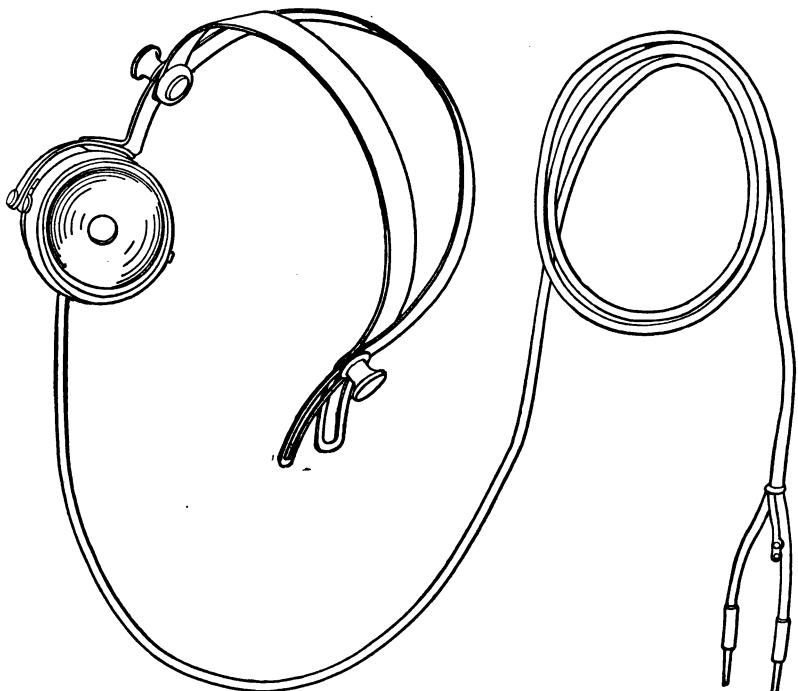

FIG. 69.

piece can be held to the ear by means of the elastic metal strap which encircles the head.

Before the Wheatstone's bridge is used the wire should be carefully calibrated. Of the several methods in use for this, that of Strouhal and Barus is best adapted to the physico-chemical laboratory.

Calibration of the Bridge-wire.—The method of calibration usually employed is that of Strouhal and Barus. Ten approximately equal resistances of German-silver wire are prepared by soldering to the ends of each length of wire a short, heavy copper wire which is afterward amalgamated. The lengths of the resistances should be so chosen that the sum of all of the resistances should nearly equal the resistance of the manganin bridge-wire. Upon a narrow strip of wood which is placed parallel to the bridge-wire are placed nine mercury-cups, 11 cm. from centre to centre. The ten re-

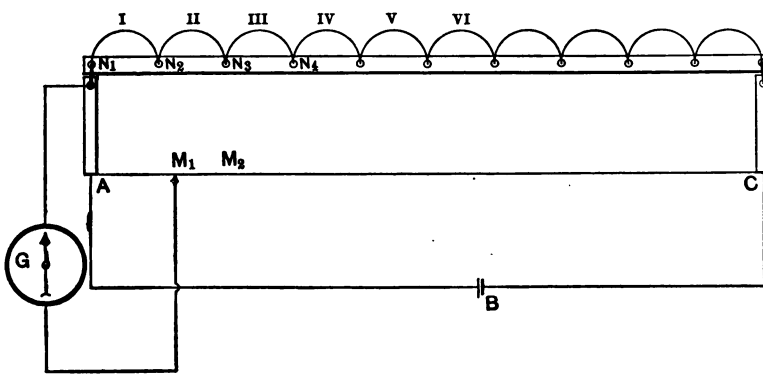

FIG. 70.

sistances are then arranged in them as shown in Fig. 70, and the connections made as indicated.

We first find a point M_1 on AC which has the same potential as N_1, this being accomplished by means of a sensitive galvanometer, G. In like manner a point M_2 is found having the same potential as N_2. The wires I and II are now interchanged, and points M_2' and M_3 are found which have the same potentials as N_2 and N_3. The calibration distances should slightly overlap, that is, the resistance of I should be so chosen that the reading for M_2, M_3 . . . shall

be a little greater than the reading for M_2', M_3'... Now I and III are interchanged, and the same operations as before are repeated. In this way the process is continued until I has replaced each resistance in succession, finally taking the place of the last one. In this way we have determined ten divisions of the wire of equal resistance, each division being nearly one-tenth of the whole.

The ten values are added together and the sum subtracted from 100 cm., the length of the bridge-wire. This difference is divided by 10 and each length is corrected by this amount, thus making the sum 100 cm.

By adding the parts we obtain the points which correspond to tenths of the wire, and the differences between these and the decimetre divisions give the corrections to be applied. Suppose that the sum of the first three lengths is 29.87, then the correction is $30.0 - 29\,87 = +0.13$. The telephone may be used in place of the galvanometer, but the results are not as accurate owing to the uncertainty as to the position of the minimum. Should the telephone be used, it must be remembered that it is not advisable to try to find the position of exact silence, but to find two points on each side of the position of minimum sound where the tones are of the same intensity. These two positions should not be more than a centimetre apart. The position of balance then lies half-way between these two points.

Conductivity Cells. — The form of cell to be used in the measurement of the conductivity of solutions depends largely upon the nature of the solution to be investigated. For solutions of low conductivity, cells must be used in which the electrodes are near together, while in the study of solutions of high conductivity it is essential that the electrodes be far apart.

In most cases the solutions with which we have to deal

are dilute, and for such solutions the cell suggested by Arrhenius is best adapted to our purpose. This cell is shown in Fig. 71. It consists of two circular parallel platinum electrodes suspended in a tall cylindrical glass cup, the cup being covered with a well-fitting ebonite cover. The electrodes are

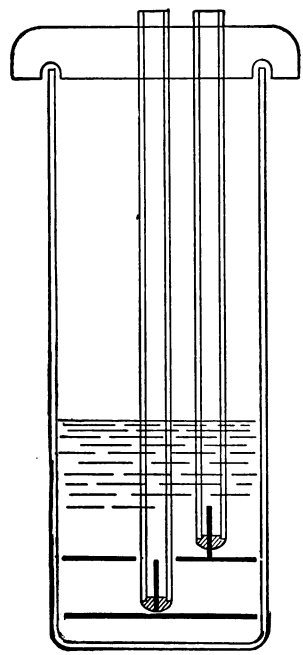

FIG. 71.

made of thick platinum foil about 4 cm. in diameter. Each electrode is welded at its centre to a short, thick piece of platinum wire, each wire being sealed into a glass tube by means of fusible enamel glass. The electrodes are held in the desired position by being fastened into the ebonite cover by means of sealing-wax. The solution to be examined is

placed in the cell so as to cover the upper electrode. The electrodes, which should fit the cross-section of the cup as nearly as possible, are held in position by the ebonite cover, in the under side of which is cut a circular groove which fits accurately over the edge of the cup. The glass tubes are filled with mercury, and by means of bent copper wires dipping into this, electrical connection is established.

In order to insure a sharp minimum in the telephone, the electrodes must be thoroughly covered with platinum-black. The platinizing is best accomplished by filling the cell with "platinizing solution" (3 grams $PtCl_4$, 0.03 gram $Pb(C_2H_3O_2)_2$ in 100 grams of water) and passing a current of 4–5 volts, with frequent changes in direction, until both electrodes are covered with a fine velvety coating of platinum-black. After platinizing they are carefully washed, and then a dilute solution of sodium hydroxide is placed in the cell, the plates inserted, and the current passed for a few moments. This procedure is to insure the removal of any of the chlorine which may have been retained by the platinum-black. The sodium hydroxide is then removed by washing with dilute hydrochloric acid, and the acid is removed by thorough washing with pure distilled water.

Since it is absolutely essential that the temperature of the cell contents remain at a definite temperature, the cell is placed in a thermostat-bath. The cell is held on a metal or ebonite shelf which is fastened to the edge of the bath, Fig. 72. Around the cell there is a tight-fitting ebonite ring which keeps the cell from slipping through the hole in the shelf. Two mercury-cups upon the shelf serve to make electrical connection between the cell and the wires to the bridge.

The following illustrations show other forms of conductivity cells, each being designed to meet special requirements, Figs. 73–76. When it is desired to protect the solvent from

the moisture of the air the forms shown in Figs. 77 and 78 may be used.

Inductorium and Telephone. — The induction-coil best suited to the needs of the physical-chemist is a small coil of few turns. The spring of the "make and break" must

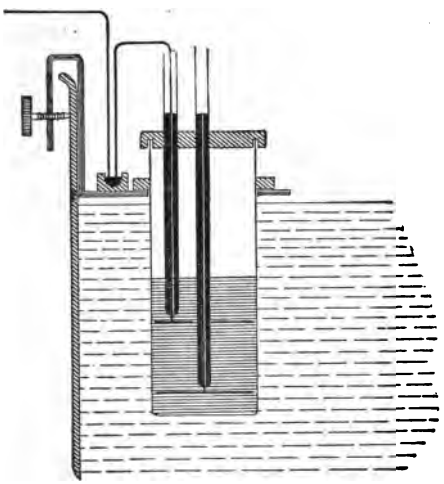

FIG. 72.

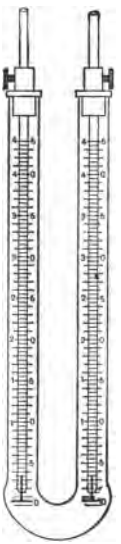

FIG. 73.

vibrate rapidly, since the telephone is more sensitive to high than to low tones. A coil designed specially for conductivity measurements is made by Morris E. Leeds of Philadelphia. This instrument has proven itself most satisfactory to the present writer and may be most heartily recommended.

The small Bell telephone or ear-piece, such as is used on house circuits, has been found to fulfil all the requirements. Since some difficulty is likely to be experienced from the sound of the coil interfering with the sound in the telephone, it is advisable to have the coil in an adjacent room or to have it covered with some insulating material, such as felt. The

unemployed ear may also be stopped with a small glass bulb. In the circuit from the storage-cell to the inductorium a switch is inserted, Fig. 79.

Resistance Capacity of the Cell.—As has been pointed out, the conductivity of an electrolyte is expressed as molecular conductivity, which is the conductivity of a gram-molecular weight of the electrolyte or the conductivity of the volume of solution containing a gram-molecular weight when placed

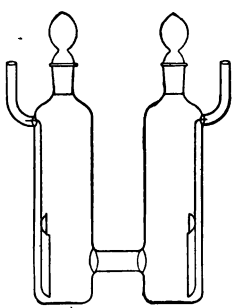

FIG. 74.

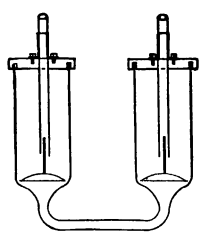

FIG. 75.

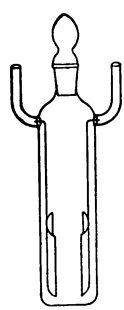

FIG. 76.

between two electrodes which are 1 cm. apart. This relation is expressed thus:

$$\mu = vs.$$

Now the conductivity as measured in a cell stands to the specific conductivity in a ratio which is dependent upon the shape and size of both electrodes and cell. This factor K has been called by Kohlrausch the *resistance capacity* of the cell. To determine K for any cell, a solution of known specific conductivity is measured and the ratio of the specific conductivity to the observed conductivity is the resistance capacity. If C is the observed conductivity of a solution of which the specific conductivity is s, then

$$K = \frac{s}{C}.$$

If C' is the conductivity of another solution having a specific conductivity s', then

$$s' = KC'.$$

By reference to the notation in Fig. 80, where the complete connections of the bridge for a conductivity measurement are

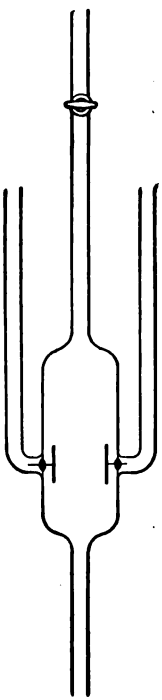

FIG. 77.

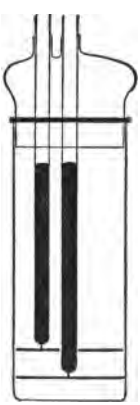

FIG. 78.

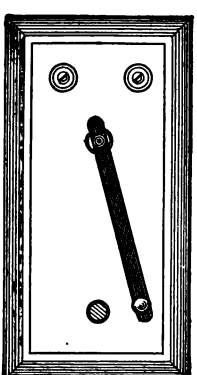

FIG. 79.

shown, the following equation will be seen to be in accordance with the law of Wheatstone's bridge:

$$C = \frac{1}{w} \cdot \frac{a}{b};$$

but

$$s = KC,$$

hence

$$s = \frac{K}{w} \cdot \frac{a}{b}.$$

Since

$$\mu = vs,$$

$$\mu = K \cdot \frac{v}{w} \cdot \frac{a}{b}.$$

Since potassium chloride can be obtained in a very pure state by repeated crystallization, it is most usually employed in determining the value of K.

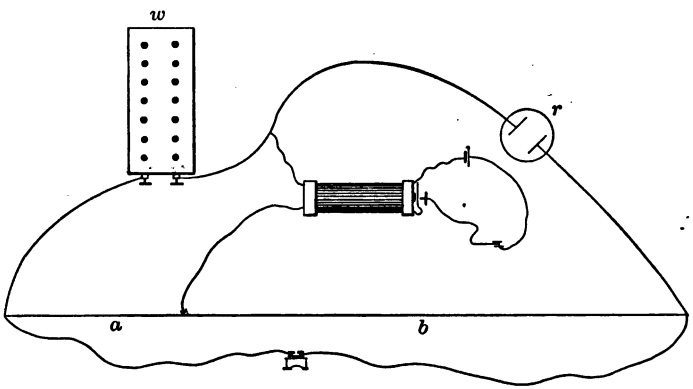

FIG. 80.

A $\frac{N}{50}$ solution of KCl has been found to have a molecular conductivity of 129.7 at 25° C. or 112.2 at 18° C. This solution contains 74.59 grams of KCl in 50 litres of solution. The value of K is then found from the formula

$$K = \mu \frac{bw}{av},$$

or at 25° C.

$$K = 129.7 \frac{bw}{50a} = 2.594 \frac{bw}{a}.$$

Carrying out a Measurement.—As a typical example of a conductivity measurement we may take the experimental determination of K.

The one-fiftieth normal potassium chloride solution is poured into the carefully cleaned cell, and the electrodes are inserted, care being taken to avoid air-bubbles clinging to the plates. The cell is then placed in the thermostat-bath, which is brought exactly to 25° C. After the cell has remained in the bath a sufficient length of time for the solution to acquire a uniform temperature throughout of 25° the cell is connected with the circuit, the switch thrown in, and by means of the variable resistance the point of minimum tone is brought near the middle of the bridge.

The resistances in the box should never be less than 20 ohms, since the telephone method is not accurate for smaller resistances. It can be shown that the bridge readings between 40 cm. and 60 cm. are the most accurate, so that it should be made a rule to try to bring the point of balance between these limits. Several readings should be taken with different resistances in the box.

By substituting these values in the equation

$$K = 2.594 \frac{bw}{a}$$

the value of the resistance capacity of the cell is found. In carrying out other conductivity measurements the procedure is the same, but the value sought is that of the molecular conductivity, K having been determined for the cell used. The results are then substituted in the equation

$$\mu = K \cdot \frac{v}{w} \cdot \frac{a}{b}.$$

A table has been compiled by Obach whereby the ratio of a to b is given for a wire 100 cm. in length. This is very

useful where many conductivity measurements are to be made.

Since the cell is to be used for a series of measurements, it is obvious that the electrodes must not be moved with respect to each other, nor must their surfaces be altered in any way. They should be cleaned with pure distilled water, and dried by washing with alcohol and ether. When not in use the electrodes should be suspended in an appropriate rack and protected from the dust. The distance between the electrodes should be varied according to the concentration of the solution. For solutions of greater concentration than $\frac{N}{200}$ the electrodes should be at least 1 cm. apart.

In making conductivity measurements every possible precaution must be taken to insure clean and well-made connections, and to exclude impurities from the solutions.

Pure Water.—Since most conductivity measurements are made upon aqueous solutions, it becomes of importance to secure the purest water possible for making the solutions.

By distilling in vacuo the purest water obtained by other methods of distillation, Kohlrausch succeeded in preparing water having a specific conductivity in vacuo of 0.04×10^{-6}.

This degree of purity cannot be attained in ordinary practice.

Nernst has proposed purifying the water for conductivity purposes by fractional crystallization.

Far more rapid and efficient is the method employed by Hulett. This consists in first distilling ordinary distilled water from potassium dichromate and sulphuric acid, and then redistilling from a solution of barium hydroxide. In this way it is possible to obtain water having a specific conductivity of from 0.7×10^{-6} to 0.8×10^{-6}. Jones and Mackay

have improved Hulett's process, so that the distillation from dichromate of potassium and sulphuric acid and from barium hydroxide becomes perfectly continuous. In this way four or five litres of water having a specific conductivity of 2×10^{-6} can be obtained daily.

In calculating the molecular conductivity of neutral substances a deduction must be made for the conductivity of the water.

This calculation is performed by multiplying the specific conductivity of the water by the molecular volume of the solution and subtracting the product from the molecular conductivity. This correction need only be applied to solutions less than $\frac{N}{50}$, since for greater concentrations the correction is much less than the experimental error. With acids and bases the impurities present in the water are likely to neutralize the acid or the base, thus causing a diminution in the conductivity. It is at once evident that the application of any correction in such cases would be absurd.

Equivalent Conductivity. — Frequently the results of conductivity measurements are expressed as equivalent conductivities instead of molecular conductivities. Equivalent conductivity is derived from molecular conductivity by dividing it by the valence. Thus the equivalent conductivity of $NaNO_3$ is the same as the molecular conductivity, the equivalent conductivity of $BaCl_2$ is equal to one-half of the molecular conductivity, and in $Al_2(SO_4)_3$ the equivalent is one-sixth of the molecular conductivity.

Denoting equivalent conductivity by λ, we have

$$\lambda=\frac{\mu}{n},$$

where n is the number of equivalents contained in a litre.

Degree of Dissociation.—It is obvious that the degree of dissociation is the ratio of the molecular conductivity at any dilution to the molecular conductivity at infinite dilution, for at moderate dilutions the molecules are only partially broken down into ions, while at infinite dilution ionization is complete. The degree of dissociation α is then expressed thus:

$$\alpha = \frac{\mu_v}{\mu_\infty}.$$

The value of μ_∞ is determined by measuring the conductivities of successive dilutions until the molecular conductivity remains constant, showing that the electrolyte is completely dissociated.

The Dissociation Constant.—Many monobasic organic acids and other slightly dissociated electrolytes exhibit a variation of molecular conductivity with change in volume. The mathematical expression of this relation is

$$k = \frac{\mu_v^2}{\mu_\infty(1-\mu_v)v},$$

where k is a constant, known as the dissociation constant. It is customary to express the dissociation constant for an acid as one hundred times the value given by the above equation, thus avoiding too small numbers, or $K = 100k$. In measuring the dissociation constant of an acid we proceed in the following manner: The strength of the acid is first determined by means of a solution of standard alkali, care being taken that the acid is not stronger than tenth-normal. A thoroughly cleaned bottle of 250 c.c. capacity is filled with the purest conductivity water, and is immersed to the neck in the thermostat bath, which is adjusted to 25° C.

An Arrhenius conductivity cell is then filled with 10 c.c.

of the approximately $\frac{N}{10}$ acid, the electrodes are inserted, care being taken to avoid air-bubbles, and the cell is then placed in the thermostat. When the contents of the cell has acquired the temperature of the bath (this usually requires twenty or thirty minutes) the conductivity of the acid solution is measured. Then 10 c.c. of water at 25° C. from the 250-c.c. bottle are introduced into the cell, and the solution made homogeneous by slowly raising and lowering the cover and electrodes. After the lapse of five minutes another measurement is made. With the pipette 10 c.c. of the solution in the cell is removed and 10 c.c. of water added in its place. After five minutes another measurement is made. This process is continued until the dilution becomes too great to permit of accurate determinations. This point is reached when the concentration becomes one-thousandth normal. Since weak acids are only very slightly dissociated, the determination of μ_∞ is accomplished by the indirect method of measuring the molecular conductivity of the sodium salt.

For the more complex acids the value of μ_∞ may be estimated with sufficient accuracy from the number of atoms in the molecule, thus avoiding the experimental determination. The following table gives the value of μ_∞ at 25° C. for complex acids with different numbers of atoms:

Acids with	12	atoms	. . . . .	$\mu_\infty = 383$
" "	15	"	. . . . .	$\mu_\infty = 380$
" "	18	"	. . . . .	$\mu_\infty = 378$
" "	22	"	. . . . .	$\mu_\infty = 376$
" "	25	"	. . . . .	$\mu_\infty = 375$
" "	30	"	. . . . .	$\mu_\infty = 374$

The Basicity of Acids.—Ostwald discovered the purely empirical relation that one-tenth of the difference between

the molecular conductivities of the sodium salt of an organic acid at dilutions 32 and 1024 is equal to the basicity of the acid. This may be represented thus: $\mu_{1024} - \mu_{32} = 10 \times$ basicity.

About 20 c.c. of a $\frac{N}{32}$ solution of pure sodium hydroxide is titrated with the dry acid of which the basicity is sought, phenolphthaleïn being used as an indicator. When the pink color has just been destroyed the $\frac{N}{32}$ solution of the sodium salt of the acid is placed in a conductivity cell and the molecular conductivity determined. The solution is then diluted with pure water to volume 1024 and the molecular conductivity again determined. The difference between the molecular conductivity at volume 1024 and the molecular conductivity at volume 32 divided by 10 gives the basicity of the acid.

Solubility by the Conductivity Method.—The saturated solution of a difficultly soluble salt may be considered as completely dissociated since the solution is so dilute. We may therefore equate μ_v and μ_∞ and write the equation for molecular conductivity thus:

$$\mu_v = \mu_\infty = K \cdot \frac{v}{w} \cdot \frac{a}{b},$$

or

$$v = \mu_\infty \cdot \frac{wb}{Ka},$$

where v is the number of litres in which one gram-molecule of the salt is dissolved.

The finely powdered difficultly soluble salt is well washed with pure conductivity water, the salt being then brought into the conductivity cell and covered with the pure water of which the conductivity is known. The contents of the cell are well shaken, the electrodes introduced, and the whole placed

in the thermostat. After sufficient time has elapsed for the cell and contents to acquire the temperature of the bath the conductivity is measured. This process is repeated until constant conductivity is obtained. If s denotes the measured specific conductivity of the solution minus the specific conductivity of the water, and λ_A and λ_C are the equivalent conductivities of the anions and cations, then the equivalent concentration per litre is $\frac{\lambda_A + \lambda_C}{1000s}$, a formula which can be readily reconciled with the preceding.

The conductivity method is also applicable to the determination of the concentration of solutions of electrolytes and to the appproximate determination of small quantities of electrolytes in mixtures or solutions with larger quantities of substances having lower conductivity.

For further information on the conductivity method the student is referred to "Das Leitvermögen der Elektrolyte," by Kohlrausch and Holborn.

CHAPTER XI.

ELECTROMOTIVE FORCE.

Clark Standard Cell.—In accordance with the decision of the International Congress of Electricians held in Chicago in 1893, the Clark cell has been made the legal standard of electromotive force. The cell consists of the system

$$- \mid Zn \mid ZnSO_4 \mid Hg_2SO_4 \mid Hg \mid +.$$

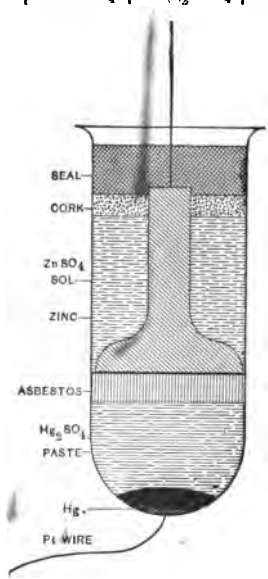

FIG. 81.

Several forms of this cell have been devised, but perhaps the most suitable for physico-chemical purposes is the Carhart-

Clark cell, which has the advantages of both portability and a lower temperature coefficient than the normal Clark cell. The arrangement of this cell is shown in Fig. 81.

Into the bottom of a glass tube 5 cm. long and 1.5 cm. in diameter is sealed a piece of No. 28 platinum wire. In contact with this wire is pure redistilled mercury. Upon this there is a layer about 1 cm. thick of pure neutral mercurous sulphate mixed with neutral zinc sulphate saturated at 0° C. This paste is then covered with a layer of purified asbestos upon which rests the electrode of pure zinc cast as shown in the figure. To the top of the zinc is soldered a thin copper wire. The zinc electrode passes through a thin disc of cork which holds the seal. This cork must be boiled for some time in distilled water to remove the tannin, then dried, and finally saturated with paraffin. The zinc sulphate solution which surrounds the zinc is introduced by means of a funnel before the zinc is inserted. The cell is finally sealed by running in a hot cement of gutta percha and Burgundy pitch with enough balsam of fir to impart fluidity.

Preparation of Materials.*—(*a*) *Mercury.*—The mercury should first be purified by causing it to pass in a fine stream through a long column of dilute nitric acid and then distilled in a vacuum.

(*b*) *Zinc.*—Only the purest redistilled zinc should be employed in making the zinc electrode.

(*c*) *Mercurous Sulphate.*—Mix the purest obtainable mercurous sulphate with a small quantity of pure mercury, and wash the whole thoroughly by agitation in a bottle; drain off the water and repeat several times. After the last washing drain off as much of the water as possible, but DO NOT DRY BY HEATING.

(*d*) *Zinc Sulphate Solution.*—Prepare a neutral saturated

* Taken from Carhart's Electrical Measurements.

solution of *pure* recrystallized zinc sulphate by mixing distilled water with approximately twice its weight of crystals of the salt, and adding zinc oxide in the proportion of about 2 per cent. by weight of the zinc sulphate crystals to neutralize any free acid which may be present. The crystals should be dissolved by heating slightly, but the solution must not be warmed above 30° C. Mercurous sulphate purified as in (*c*) is added in the proportion of about 12 per cent. by weight of the zinc sulphate crystals to neutralize the free zinc oxide remaining. The solution is then filtered and cooled to 0°. Crystals should form as the solution cools.

(*e*) *Paste of Mercurous and Zinc Sulphates.*—Two or three parts by weight of mercurous sulphate are added to one part by weight of mercury.

If the sulphate is dry, it is mixed with a paste consisting of zinc sulphate crystals and a concentrated zinc sulphate solution, so that the whole constitutes a stiff mass, which is permeated throughout by zinc sulphate crystals and globules of mercury. If the mercurous sulphate, however, is not dry, only zinc sulphate crystals are to be added; care must be taken, however, that the zinc sulphate crystals are in excess and are not dissolved after long standing. The mercury must in this case also permeate the paste in little globules. It is advantageous to crush the zinc sulphate crystals before using, since the paste can be beter manipulated.

Temperature Coefficient.—The temperature coefficient of the Carhart-Clark cell is one-half of that of the Clark cell. The equation connecting the E.M.F. and the temperature for the Carhart-Clark cell is

$$E_t = 1.440\{1 - 0.000387(t-15) + 0.0000005(t-15)^2\}.$$

For ordinary room temperatures this formula may be simplified thus:

$$E_t = 1.440 - 0.00056(t-15).$$

Weston Standard Cell.—Another form of standard cell (Fig. 82) frequently employed in the physico-chemical

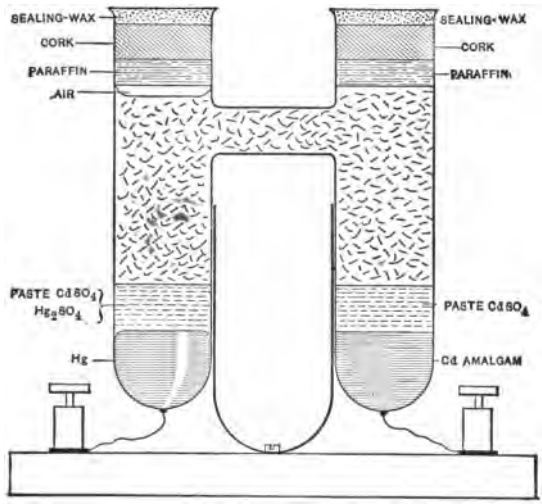

FIG. 82.

laboratory is that invented by Edward Weston. The cell is constructed upon the scheme:

$$- \mid Cd \mid CdSO_4 \mid Hg_2SO_4 \mid Hg \mid +.$$

The H form of cell has been chosen as best.

Into the bottom of each limb is sealed a platinum wire. In one limb is an amalgam of cadmium, while in the other limb is mercury and a paste of mercurous sulphate mixed with a solution of cadmium sulphate. The two limbs are connected through a solution of cadmium sulphate. The E.M.F. of the cell is 1.019 volts, and the temperature coefficient is 0.01 per cent. per degree centigrade.

Helmholtz One-volt Cell.—A cell of exactly one volt electromotive force is very useful for many purposes. The cell shown in Fig. 83 was devised by Helmholtz in 1882.

The electrodes consist of amalgamated zinc and mercury, the mercury being covered with mercurous chloride and a solution of zinc chloride (sp. gr. 1.409).

Since zinc chloride is usually basic, enough hydrochloric acid should be added to the concentrated aqueous solution to just dissolve the white residue. Some granulated zinc should also be added to the zinc chloride solution in order to

FIG. 83.

remove any cadmium which may be present. When the cell is assembled it will give an E.M.F. of 1 volt $\pm$ 0.01. The temperature coefficient is so small as to be negligible.

The scheme of the cell is

$$- \mid Zn \mid ZnCl_2 \mid Hg_2Cl_2 \mid Hg \mid +.$$

Lippmann Electrometer.—This instrument is best suited to physico-chemical purposes, since it is small and very slightly affected by external disturbances. It is based upon the principle that the surface tension of mercury in contact with dilute sulphuric acid changes when there is a change in potential between the points of contact. One surface of contact is large while the other is very small, since when there is a difference of potential between these surfaces it distributes itself in the ratio of the surfaces and the smaller

electrode is thus affected almost exclusively. In the electrometer devised by Lippmann the small electrode is caused to assume a definite position under the action of the molecular force. When a difference of potential is introduced, the resulting movement takes place almost entirely at the smaller surface, thus making it possible to measure the potential difference.

A very convenient form of electrometer is shown in Fig. 84. The glass apparatus consists of a small flask, *b*,

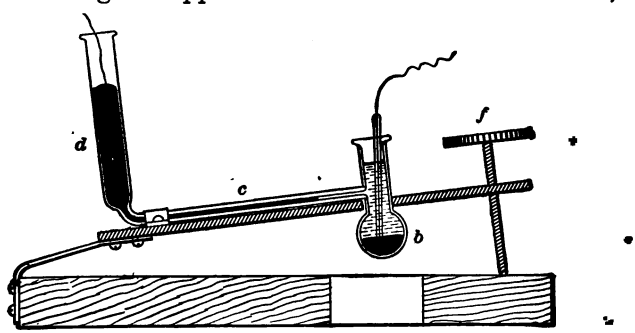

FIG. 84.

into the neck of which is fastened a small capillary tube, *c*, which terminates in a larger tube, *d*. This is attached to a thin piece of wood, which is fastened to a heavy base-board at one end by means of a spring-hinge. The other end of the strip is provided with an adjusting-screw, *f*, by means of which the capillary can be inclined at any desired angle to the base-board. Beneath the capillary *c* there is placed a millimetre scale by means of which the position of the end of the mercury column may be accurately noted.

The electrometer is made ready for use by first placing mercury in *d* and *b* and then pouring dilute sulphuric acid (1 : 6 by volume) into *b*. Connection with the mercury is made by means of two platinum wires, the wire in *b* being

protected from contact with the acid by means of a glass tube fused over it. These wires are fastened to two screw terminals. The binding-screws are connected by a wire, and a drop of mercury is caused to pass from *d* to *b*. By

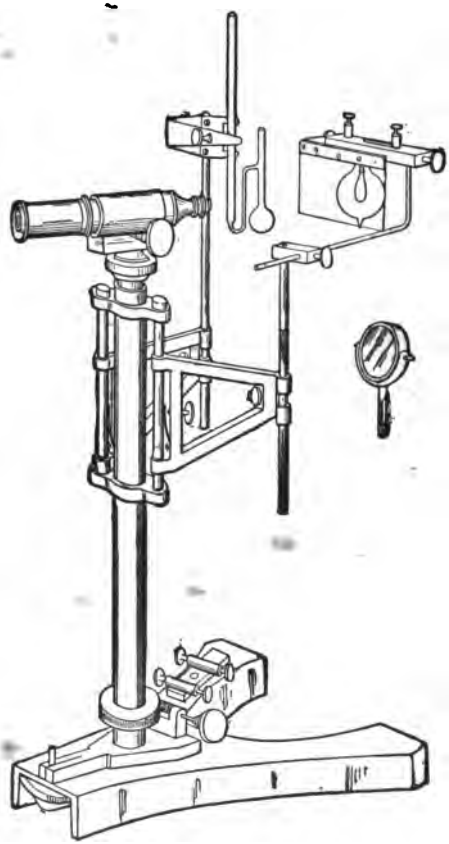

FIG. 85.

inclining the apparatus and manipulating the screw *f* the mercury thread can be brought near the end of the capillary. The greater the inclination the more rapidly can the elec-

trometer be adjusted, though the instrument becomes less sensitive with increase in the angle of inclination. By adjusting the amount of mercury in *d* the sensitiveness can be controlled. A deflection of five scale divisions for 0.01 volt is very convenient.

A more sensitive form of Lippmann electrometer is shown in Fig. 85. With this instrument five scale divisions correspond to 0.001 volt. The increased sensitiveness is due to the capillary being vertical. The position of the mercury thread is read by means of a small microscope magnifying about 30 diameters and provided with a scale in the eyepiece.

The mercury column is illuminated either by a small electric incandescent lamp or by a concave mirror such as is used on microscopes.

Since it is necessary to keep the mercury in the two arms of the electrometer in electrical connection except at the instant of making a measurement, a key devised by Ostwald is extremely useful. This is shown in Fig. 86. It consists

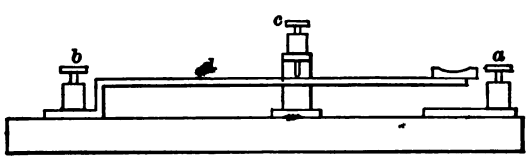

FIG. 86.

of a strip of brass, *d*, connected at one end with the binding-screw *b* and at the middle with the screw *c*. Upon pressing the strip downward connection is established between *b* and *a*, while connection with *c* is broken. The terminals *b* and *c* are kept permanently in connection with the terminals of the electrometer, while *a* is connected with the potential to be measured.

The Measurement of Electromotive Force.—Of the many different methods which have been devised for the measure-

ment of E.M.F., the Poggendorff *compensation method* is best adapted to the requirements of the physical-chemist. In this method the E.M.F. to be measured is opposed to a variable E.M.F., the latter being altered until the one cancels the other. The general scheme of the method is shown in Fig. 87.

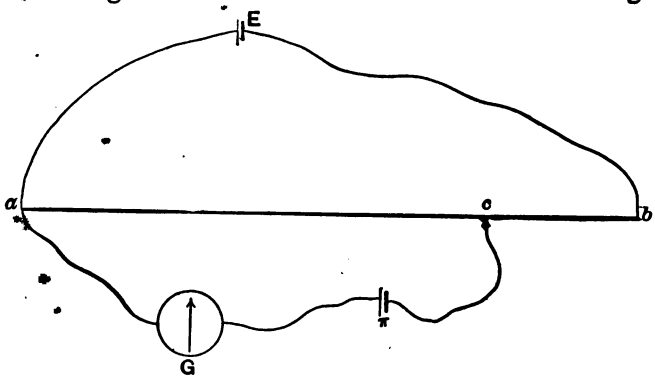

FIG. 87.

A constant element, E, having a greater E.M.F. than that to be measured, is closed through the resistance ab. The element π of which the E.M.F. is sought is connected through the galvanometer or electrometer G with a and the sliding contact c. The contact c is moved along ab until the instrument G indicates zero. Call this position of c, p_1. Now for π we substitute a standard cell (Carhart-Clark or Weston element) S, and again move c along the wire until a balance is obtained. Denote this position by p_2. Then we have the proportion:

$$\text{E.M.F. of } \pi : \text{E.M.F. of } S = ap_1 : ap_2,$$

or

$$\text{E.M.F. of } \pi = \frac{\text{E.M.F. of } S \times ap_1}{ap_2}.$$

It is obvious that there will always be some point between a and c where the potentials of E and π will balance provided the potential of E is greater than that of π.

Owing to the impossibility of obtaining a substance in the form of a wire having a uniform resistance of several thousand ohms, *ab* is replaced by certain forms of resistance devised by Ostwald. Into an ebonite plate, Fig. 88, are

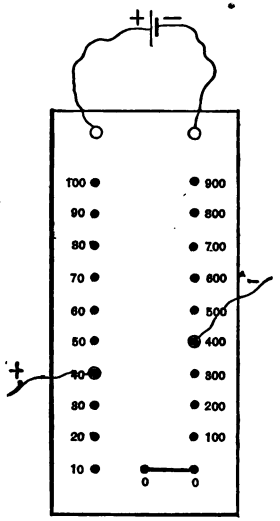

FIG. 88.

screwed twenty-one brass pegs and two terminals. By means of heavy copper wires the terminals are connected to the adjoining pegs, and in a similar manner the pegs marked 0 are connected with each other.

Underneath the ebonite plate, the pegs, all of which project through the plate, are connected in the following manner: one series of pegs are connected with each other through wire resistances of 100 ohms each, the other series through similar resistances of 10 ohms each.

In this arrangement we then have one row of 9×100 ohms and another row of 10×10 ohms, making the total resistance 1000 ohms.

Against each peg is written the resistance reckoned from the zero peg. The plate is finally screwed on a box to protect the resistances from injury. Two tubular, slit caps provided with insulated tops and small binding-screws fit over the pegs and serve to make connections with the resistances in the box. This box as made by Köhler of Leipzig is shown in Fig. 89.

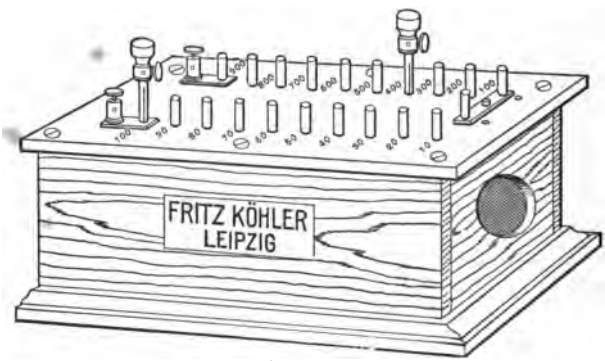

FIG. 89.

Before proceeding to the description of the complete connections for the measurement of E.M.F. by the compensation method an important accessory must be described. It frequently happens that differences of potential greater than one volt have to be measured, in which case it is necessary to connect one cap or both of the resistance-box just described to a small battery of several one-volt elements. This arrangement, shown in Fig. 90, is also due to Ostwald. Five one-volt Helmholtz elements are arranged on a board with the pegs *a*, *b*, *c*, *d*, *e*, *f*, *g* placed as shown in the sketch. The pegs *f* and *g* are connected with each other by means of a heavy copper wire and also with the zinc terminal of the nearest element. The peg *e* is connected with the platinum electrode of the same element and also with the zinc of the

next element in order. This method of connection is carried to the end of the board where the platinum of the fifth element is connected with *a*. This is also provided with caps similar to those used on the resistance-box. If the

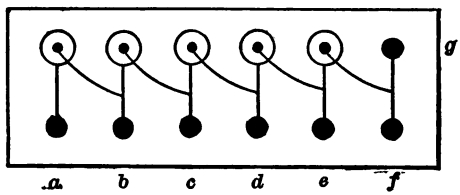

FIG. 90.

caps are on *f* and *g*, there is no difference of potential obtained; if on *e* and *f*, the battery gives 1 volt; if on *d* and *f*, 2 volts; and finally *a* and *f* give 5 volts.

Each element can be opposed to the whole potential of the resistance-box so that the E.M.F. at the terminals can be made equal to 1 volt.

The elements can also be compared with each other. All of the connections of the apparatus for the measurement of electromotive force are shown in Fig. 91. A primary cell, usually a Le Clanché element, *L*, is connected to the resisttance-box *R* through a secondary resistance *W*, which suffices to reduce the electromotive force of the Le Clanché cell to exactly 1 volt. From the caps of the box *R* the wires connect with the Lippmann electrometer *E* and the cell, π, to be measured. In the illustration the five-volt battery is included in this last portion of the circuit. The second terminal of π is connected to earth. The earth conductor is also connected with the electrometer and the middle terminal of the electrometer key *K*, the principal terminal of which is connected with the other terminal of the electrometer.

The remaining terminal of the electrometer key is connected with the resistance-box by the cap *b*.

On pressing the key, the circuit *EbacdπE* is closed, and if the mercury column in the electrometer moves, the poten-

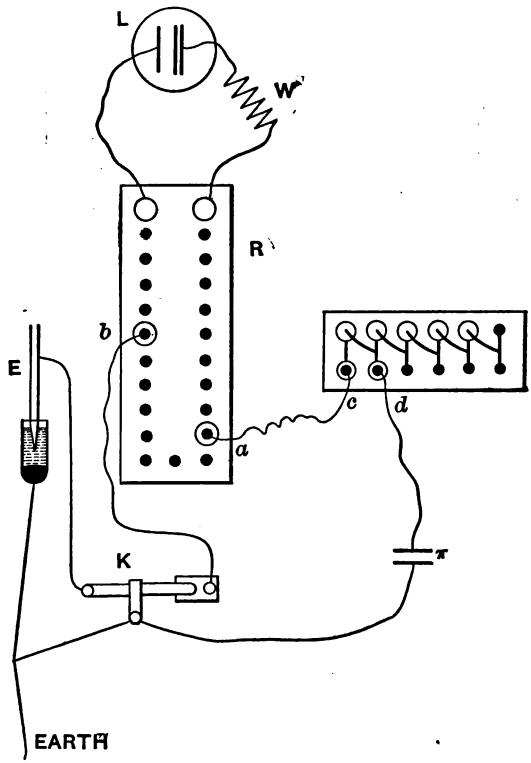

FIG. 91.

tial difference is changed by moving the caps on the resistance-box until finally a potential difference is obtained which exactly compensates the potential difference of π, when there is no motion of the mercury in the electrometer. It will be noted that every step on one side of the resistance-

box gives a rise of potential of 0.01 volt, while every step on the other side corresponds to 0.1 volt. After exactly balancing the E.M.F. sought against the Le Clanché cell, the standard cell is substituted for the cell under investigation and a new balance is obtained.

The desired E.M.F. is then calculated by the equation given on p. 188.

Potential Differences.—In all galvanic elements the total difference of potential is the algebraic sum of the potential differences at the points of contact of the various substances composing the galvanic system.

In the system

$$-\text{Zn} \mid \text{ZnSO}_4 \mid \text{CuSO}_4 \mid \text{Cu}+$$

the sources of potential are (*a*) between zinc and zinc sulphate (*b*) between copper and copper sulphate; (*c*) between zinc sulphate and copper sulphate; and (*d*) between zinc and copper. Of these four sources of potential the most important are the differences existing between the metals and the solutions of their respective sulphates. Second in magnitude is the potential difference between the two solutions, while of trivial importance is the potential between the two metals.

The potential differences existing between a metal and a solution depend not only on the nature of the metal, but also upon the concentration of the metal ions in the solution. The condition of the surface of the metal has often a marked influence upon the electromotive force. It is advisable when possible to use the metal in the form of an amalgam, thus insuring a well-defined surface. The electromotive force of an amalgam is nearly the same as that of the pure metal, but does undergo some change with the strength, so that the concentration must always be ascertained.

The most convenient means of preparing an amalgamated

electrode is to pass an electric current through a solution of the salt of the metal, using mercury as the cathode and a platinum wire for the anode. By including a silver voltameter in the circuit the exact quantity of metal deposited can be calculated.

The potential differences existing between solutions is wholly dependent, as Nernst has shown, upon the relative velocities of the ions. In the system cited above, copper and zinc having nearly equal velocities of migration, the potential

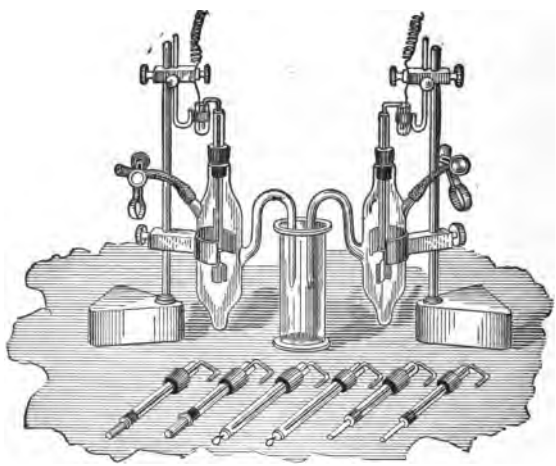

FIG. 92.

difference is practically negligible. In the investigation of potential differences, the electrolyte is poured into a tube through the stopper of which passes the electrode; to the side of the tube is sealed a siphon-tube which serves to connect it through an intermediate vessel (beaker) with a similar tube also provided with an electrode. This apparatus is shown in Fig. 92.

Normal Electrodes.—In order to measure the difference

of potential between an electrode and an electrolyte it is necessary to employ another electrode and generally another electrolyte. For this reason it is advisable to use the same electrode and same electrolyte in all measurements of differences of potential between metals and their electrolytes. Such a standard electrode is known as a *normal electrode.*

The most satisfactory of several proposed normal electrodes is that devised by Ostwald and shown in Fig. 93.

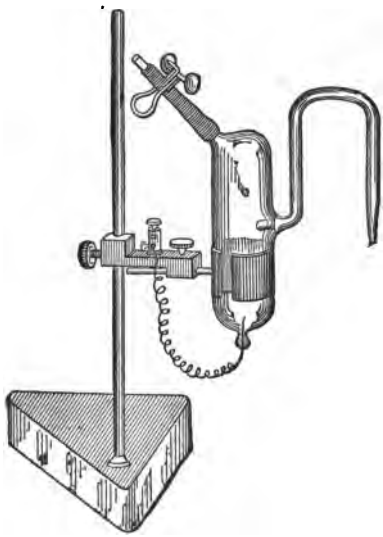

FIG. 93.

Pure mercury is poured on the bottom of the vessel, and upon this there is placed a layer of mercurous chloride and then a normal solution of potassium chloride. By means of the platinum wire which is sealed into the bottom of the vessel connection is established with the mercury, while by means of the siphon-tube containing potassium chloride solution the normal electrode can be put in communication with the electrolyte under investigation. The difference of potential

between the mercury and potassium chloride is 0.56 volt at room temperature, or more exactly

$$\pi_{Hg} - \pi_{nKCl} = +0.56 + 0.0006(t - 18°).$$

It is to be noted that the mercury is positive to the potassium chloride. The following example will make clear the use of the normal electrode: It is desired to determine the potential difference between zinc and a normal solution of zinc sulphate. The system then takes the form

$$Zn - n ZnSO_4 - n KCl, HgCl - Hg.$$

Against the normal electrode we find $\pi = 1.08$ volts, the current flowing in the direction of the arrow. From the fundamental theory of the cell we know the total E.M.F. to be given by the equation

$$\pi = (\pi_1 - \pi_2) = \frac{RT}{2e_0} \log_\varepsilon \frac{P}{p} - \frac{RT}{e_0} \log_\varepsilon \frac{P'}{p'},$$

where P and p are the solution tension and osmotic pressure of the zinc ions respectively, and where P' and p' are the corresponding values for mercury. We then have

$$1.08 = \frac{RT}{2e_0} \log_\varepsilon \frac{P}{p} + 0.56,$$

or

$$\frac{RT}{2e_0} \log_\varepsilon \frac{P}{p} = (1.08 - 0.56) = +0.52 \text{ volt.}$$

In other words, zinc is positive against a normal solution of its sulphate and gives an electromotive force of 0.52 volt. It is to be borne in mind that the sign always refers to the potential of the electrolyte against the electrode.

Calibration of a Voltmeter.—In order to use a voltmeter for accurate measurements it is essential that it should be carefully calibrated. This is accomplished by balancing the

electromotive force of one or more standard cells against a fraction of the potential differences applied to the terminals of the voltmeter, this fraction being determined by means of reliable resistances. In Fig. 94 are shown the connections and arrangements of the apparatus. Two large resistance-boxes R and R' are employed, R having a total resistance of

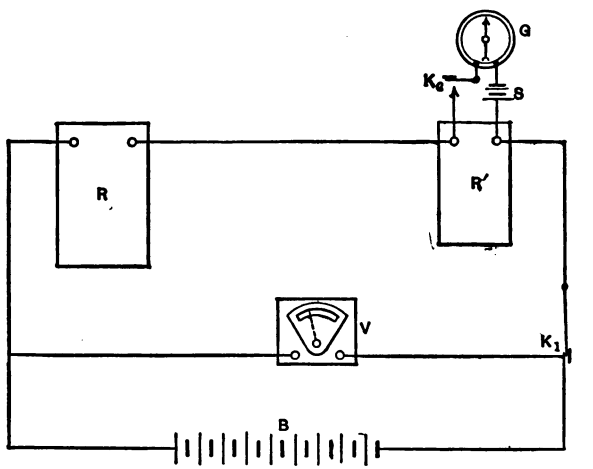

FIG. 94.

100,000 ohms and R' having a range sufficiently great to permit of accurately calibrating the whole scale of the voltmeter. The requisite potential difference is furnished by means of the storage-battery B. V is the voltmeter, G the galvanometer, S the battery of standard cells, and K_1 and K_2 are keys.

The method of calibration consists in varying the resistances R and R' until, on closing first K_1 and then K_2, the galvanometer shows minimum deflection. While approximating the values of R and R' which will give minimum deflection, it is advisable to insert a high resistance in the shunt circuit which contains the galvanometer and the stand-

ard cells. If no current passes through the galvanometer, the potential difference of the standard cells is the same as that of the binding-posts of the resistance-box R'. The voltmeter is now read. Then we have

$$V = wE\frac{R+R'}{R'},$$

where V is the number of volts, and E is the electromotive force for the standard cell, and where n is the number of cells. The difference between V and the reading on the voltmeter will be the error for that part of the scale. The voltage is then altered and balance again restored and a new reading taken. In this manner the entire scale of the voltmeter is calibrated.

CHAPTER XII.

MEASUREMENT OF CURRENT.

Of the various methods for measuring the electric current, that based upon electrolysis is best adapted to the requirements of the physical-chemist.

Faraday's law may be summarized by the equation

$$m = Kit,$$

where m is the mass of metal deposited by current i in time t, and where K is a proportionality factor known as the *electrochemical equivalent.*

It is at once apparent that if the mass of deposited metal, the electrochemical equivalent for that metal, and the time during which electrolysis is taking place be known, then the strength of current is determined by the equation

$$i = \frac{m}{Kt}.$$

The electrolytic cell by which current strength is determined is known as a *voltameter.*

Several different voltameters adapted to such conditions as are likely to be met with in the physico-chemical laboratory will be described.

The Silver Voltameter (Fig. 95).—For currents as large as one ampere the cathode should consist of a platinum dish about 10 cm. in diameter and 5 cm. in depth. The anode should be a circular plate of pure silver 2 mm. thick and

having an area of about 30 sq. cm. This is placed in a horizontal position near the surface of the liquid in the platinum dish, the supporting wire being also of platinum.

The anode should be covered with a wrapping of fine muslin or filter-paper to prevent any disintegrated particles of silver, silver oxide, or carbon from falling into the dish.

The platinum dish rests upon an insulated copper sup-

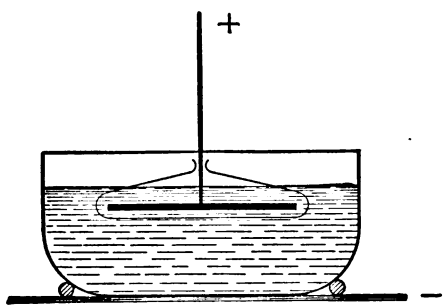

FIG. 95.

port which serves to connect it with the negative terminal of the source of current, while the anode wire is directly connected with the positive terminal. The electrolytic bath should consist of a neutral solution of silver nitrate containing 15 parts of pure silver nitrate to 85 parts of pure redistilled water. The method of carrying out a measurement is as follows: The platinum dish is washed with nitric acid and then with distilled water, and then heated to redness over a Bunsen burner, after which it is allowed to cool in a desiccator and then carefully weighed. The copper support is cleaned, and the dish is placed upon it. The dish is then nearly filled with the silver nitrate solution, and the anode immersed so that the silver plate is completely covered with the solution. The anode is then connected with the positive terminal, and the circuit closed by means of a

key. The time is accurately noted at which the circuit is closed. The current is then allowed to pass for at least half an hour, the time being taken again when the current is broken. It is evident that the clock or watch employed must be a reliable time-keeper. The solution is now poured out of the dish, the silver deposit washed several times with distilled water, and the dish filled with distilled water is set aside for six hours. The dish is then emptied and again washed with distilled water, the washings being collected and tested for silver nitrate with hydrochloric acid. If no cloudiness appears, the dish is washed with absolute alcohol and dried in an air-bath at 150° C. It is then cooled in a desiccator and weighed. The gain in weight gives the silver deposited. The current in amperes is then found by substituting in the equation

$$i = \frac{m}{Kt},$$

where $K = 0.001118$, where t is expressed in seconds, and where m is expressed in grams. Instead of dividing by the time of deposit in seconds and by 0.00118, the time may be expressed in hours and fractions thereof, and K may be made equal to 4.025.

Copper Voltameter. — When large currents are to be measured the silver voltameter is replaced by the copper voltameter, since the size of silver plates required would make the former too expensive. While the copper voltameter is by no means as accurate an instrument as the silver voltameter, owing to the smaller electrochemical equivalent and the partial oxidation of the deposited metal, yet it has the advantage of easier manipulation owing to the firmly adherent deposit of copper.

For large currents the copper plates need be only one-

fifth as large as the silver plates required for the same current. About 50 sq. cm. per ampere is sufficient for good results with the copper voltameter. The copper voltameter consists of two plates of copper suspended in a copper solution contained in a glass vessel. The solution to be employed is the following:

Copper sulphate	15 grams
Sulphuric acid	5 "
Alcohol	5 "
Water	100 "

The cathode plate before use should be carefully smoothed at the edges, the corners should be rounded and the surface of the plate should be polished with very fine sandpaper. After this treatment the plate should be thoroughly washed with distilled water and then dried on clean heavy filter-paper. The plate should be very gently heated before placing in the desiccator preparatory to weighing.

The process of determining the current strength is exactly analogous to that for the silver voltameter. The electrochemical equivalent for copper is 0.0003294 if the time be reckoned in seconds, or 1.1858 if in hours.

The Titration Voltameter.—The titration voltameter of Kistiakowsky is intended for the measurement of very small currents where the experimental error due to washing and drying the cathode in the silver voltameter would be appreciable. The arrangement of this voltameter is shown in Fig. 96. An upright glass tube open at the top and closed at the bottom with a stop-cock is provided with two electrodes, the upper electrode being of platinum, while the lower one consists of a rod of silver soldered to a copper wire, the copper wire and a portion of the silver rod being inclosed in a glass tube the end of which is closed with sealing-wax.

The silver rod serves as the anode. The tube is about three-fourths filled with 15–20% solution of potassium nitrate, and the remainder of the tube is filled with $\frac{N}{4}$

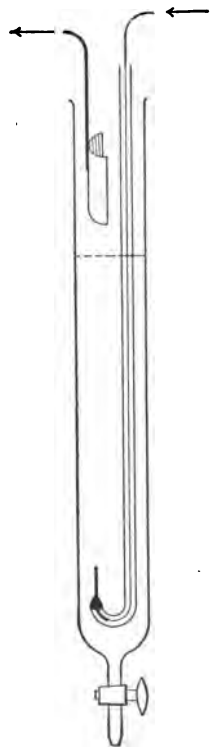

FIG. 96.

nitric acid, taking care not to mix the two solutions. The current is now passed through in the direction of the arrows, the time of closing and opening the circuit being accurately noted. When the current has been broken the stop-cock is opened and the contents of the apparatus washed out into a beaker. The content of silver is then determined either

volumetrically or gravimetrically. Each equivalent of dissolved silver corresponds to 96,540 coulombs. The current should not be allowed to flow for more than five hours, since through diffusion and convection silver is liable to separate on the cathode. Before using the voltameter the silver rod should be freshly coated with silver by electrolyzing in a bath of potassium-silver cyanide. The maximum current strength which can be measured with this form of voltameter is 30 milliamperes per square centimetre of anode.

CHAPTER XIII.

MEASUREMENT OF THE DIELECTRIC CONSTANT.

THE method about to be described is due to Nernst and is unquestionably the most satisfactory for the physico-chemical laboratory. In Fig. 97 let I be a small inductorium,

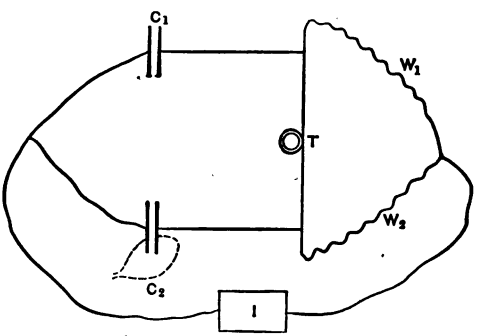

FIG. 97.

W_1 and W_2 two non-inductive resistances, c_1 and c_2 two thoroughly insulated condensers having capacities c_1 and c_2 respectively, and T a telephone. The condition for silence in the telephone is

$$W_1 : W_2 = c_2 : c_1.$$

If we make $W_1 = W_2$, arranging c_2 as an adjustable condenser, this method enables us to compare the capacity c_1 with another and hence to determine the dielectric constant. If a is the capacity of the "measuring-condenser," c_1 the capacity of an air-condenser which gives a minimum sound in the

telephone, b the corresponding value when the condenser is filled with an insulating substance of which the dielectric constant is D_x, then we have

$$D_x = \frac{b}{a}.$$

This method gives poor results or fails entirely if the substance of which the dielectric constant is sought conducts even slightly.

It is possible, however, to obtain correct values for poor conducting substances if the conductivity of the condenser c_1 is compensated by inserting a like conductivity in the measuring-condenser.

If the conductivity of the condenser c_1 is W_4, then the condition for silence in the telephone is

$$c_1 = c_2 \quad \text{and} \quad W_3 = W_4.$$

Apparatus.—The arrangement of the apparatus is shown in Fig. 98; I is the inductorium; W_1 and W_2 two parallel resistances; W_3 and W_4 two shunt resistances; c_1 and c_2 the measuring-condensers; c the vessel for containing the liquid under investigation, which through the contacts e_1 and e_2 is connected first to c_1 and then to c_2. To insure a sharp tone-minimum in the telephone all parts of the apparatus must be carefully insulated. The electrolytic resistances W_1 and W_2, which are directly connected with the induction apparatus, consist of two vertical glass tubes about 13 cm. long and 0.5 cm. in diameter, each provided with well-blackened platinum electrodes, the upper electrodes being adjustable.

The electrolytic resistance consists of the following solution:

Mannite	181 grams
Boric acid	62 "
Water	1500 "

This solution is chosen because of its very small temperature coefficient.

The measuring-condenser consists of two strong rectangular brass plates 8 cm. wide and 12 cm. long. The capacity

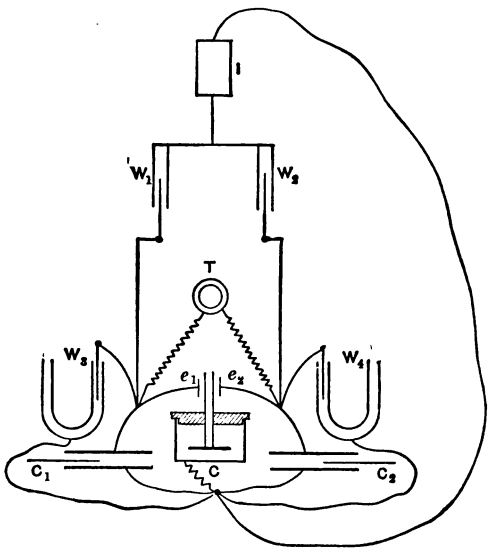

FIG. 98.

was increased through inserting a glass plate provided with a vernier.

For compensation within wider limits the additiona shunt-resistances W_3 and W_4 are included in the circuit parallel to the measuring-condenser.

This shunt-resistance, Fig. 99, consists of a narrow tube r_1, and a wide tube r_2 into the lower end of which is fused an electrode *e*. The positions of the other electrodes in r_1 and r_2 can be adjusted by means of a screw and divided scale.

The liquid to be investigated is placed in the measuring-vessel. This is shown in Fig. 100. The capacity of the

vessel was determined, as in the determination of resistances, by calibration with a liquid of known dielectric constant. The following liquids are well adapted to the purpose:

	D
Ether	4.12
Benzene	2.258

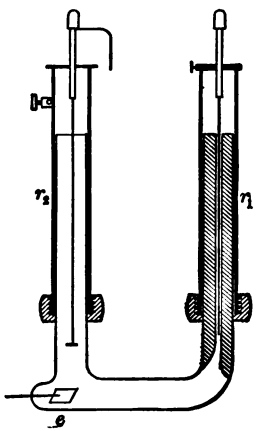

FIG. 99.

The small telephone must be provided with a well-insuated handle.

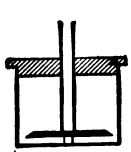

FIG. 100.

Carrying Out a Determination.—The determination of the dielectric constant by the Nernst method divides itself into three parts:

(1) *Establishment of the Equality of Resistances W_1 and W_2.*—The vessel C and the resistances W_3 and W_4 are removed

and W_1 and W_2 are tested for equality by adjusting the measuring-condensers until the minimum in the telephone is obtained. The connections are then changed so that W_2 is connected with O_1 and W_1 is connected with O_2. Then the resistances W_1 and W_2, and also the condensers, are each slightly altered and the minimum is again obtained. This process is continued until no further change in the adjustment of the condensers is necessary.

(2) *Calibration of the Measuring-condenser.*—The empty measuring-vessel is brought to such a capacity by means of a small glass plate of proper thickness (about 1 mm.) that by connecting it to e_2 it is necessary to draw out the condenser c_2 about 1 cm. The left-hand condenser is displaced to the minimum position while the right-hand stands at 0; the measuring-vessel is then connected at e_2 and the resulting alteration of the right-hand condenser is measured. Then the measuring-vessel is placed in the middle between e_1 and e_2, the left-hand condenser put in while the right-hand stands at 1, the vessel again added, etc., etc. If the right-hand condenser is without error of calibration, the addition of the vessel must always correspond with an equal displacement (say 1 cm.); from the deviations, the corrections for the scale divisions are at once obtained. The values of the scale divisions of the left-hand condenser are then determined through direct comparison with the right-hand condenser.

(3) *Determination of the Dielectric Constant.*—The empty vessel C is placed in the middle between e_1 and e_2, the right-hand condenser placed at 0, and the left adjusted until the minimum in the telephone is obtained. The shunt-resistances W_3 and W_4 are then altered until the telephone minimum is rendered as sharp as possible. With liquids of slight conductivity one should use only the narrow resistance-tube.

The vessel C is connected with e_2, the right-hand condenser plate adjusted until the minimum is again obtained. This gives the condenser setting, s_2.

The same measurement is repeated with the vessel C connected to e_1. This gives the condenser setting s_1. The vessel C is now filled with the calibration liquid, and the condenser settings σ_2 and σ_1 with the right- and left-hand condensers are obtained.

The vessel is then filled with the liquid to be investigated, and in exactly the same manner the positions s_2 and s_1 are obtained. If, owing to the conductivity of the liquid, the telephone minimum ceases to be sharp, this may be restored through adjustment of the shunt-resistances W_3 or W_4.

The dielectric constant is calculated from the data experimentally obtained, thus:

$$D=(D_0-1)\frac{S-s}{\sigma-s}+1,$$

where D = dielectric constant of liquid;

D_0 = dielectric constant for calibration-liquid;

$s=\frac{s_2+s_1}{2}$ = position of measuring-condenser for the empty vessel C.

$\sigma=\frac{\sigma_2+\sigma_1}{2}$ = position of measuring-condenser for the vessel C filled with calibration-liquid;

$S=\frac{S_2+S_1}{2}$ = position of measuring-condenser for the vessel C filled with liquid under investigation.

According to Maxwell's theory the index of refraction is equal to the square root of the dielectric constant, or

$$n=\sqrt{D}.$$

This relation has been shown to hold very satisfactorily. Nernst has pointed out that the greater the dielectric constant the greater the dissociating power. That this is of more than limited application may be seen by a comparison of tables of dissociating power of solvents and their dielectric constants.

CHAPTER XIV.

CHEMICAL KINETICS.

FROM the law of mass action the general reaction

$$n_1A_1+n_2A_2+\ldots \rightleftarrows n_1'A_1'+n_2'A_2'+\ldots$$

may be written

$$Kc_1^{n_1}c_2^{n_2}\ldots \rightleftarrows K'c_1'^{n_1'}c_2'^{n_2'}\ldots$$

Since the velocity of a reaction is proportional to its constant, K, the total velocity is equal to the algebraic sum of the velocities in the two directions, or

$$V=v-v'=Kc_1^{n_1}c_2^{n_2}\ldots -K'c_1'^{n_1'}c_2'^{n_2'}.$$

If the concentration of the substance being formed is increased by dc in the time dt, then

$$\frac{dc}{dt}=Kc_1^{n_1}c_2^{n_2}\ldots -K'c_1'^{n_1'}c_2'^{n_2'}\ldots$$

Since the constants K and K' are functions of the temperature, it follows that the above equation holds only when the reaction is isothermal.

If there are present four substances initially, that is, at $t=0$, and the respective concentrations are a_1, a_2, a_1', a_2', and x molecules of a_1 and a_2 are decomposed at the time t, then

$$\frac{dx}{dt}=K(a_1-x)(a_2-x)-K'(a_1'+x)(a_2'+x).$$

This equation may be very much simplified since most reactions are nearly complete in one direction, so that the second term may be omitted and we may write

$$\frac{dx}{dt}=K(a_1-x)(a_2-x).$$

Chemical reactions are divided into *orders*, the order of a reaction being determined by the number of substances which undergo change. It has been found by experiment that there is no chemical reaction of higher order than the third.

Reaction of the First Order.—The equation for a first-order reaction is

$$\frac{dx}{dt}=K(a-x),$$

which upon integration gives

$$K=\frac{1}{t}\log_e\frac{a}{a-x}.$$

Inversion of Cane-sugar.—The reaction

$$C_{12}H_{22}O_{11}+H_2O=2C_6H_{12}O_6$$

is an example of this type of reaction, the only substance undergoing change being the cane-sugar, since the water is present in such large excess that its mass remains practically unchanged.

A solution of cane-sugar is prepared by dissolving 200 grams of sugar in distilled water and diluting to 1000 c.c. The solution is then filtered into a clean, dry bottle and warmed in the thermostat to 25° C. A normal solution of pure hydrochloric acid is also prepared and warmed to 25° in the thermostat.

The Lippich polarimeter is made ready and the polarizing tube warmed to 25° by circulating water at that temperature through the jacket. The polarization-tube is carefully cleaned and dried and one of the plates is screwed on, then 10 c.c. of the sugar solution is mixed with 10 c.c. of the acid, the mixture is poured into the tube and the other plate screwed on, taking precautions to exclude air-bubbles. The tube is then placed in the polarimeter and observations are commenced. During the first stages of the inversion, readings are taken *every minute* until five readings have been taken, the mean of which is taken as the time of the third reading.

The readings are then taken every thirty minutes for five hours, after which the solution is allowed to stand for a period of time ten times as great as that required for half-inversion of the sugar, when the final reading is taken.

If β_1 and β_2 are the rotations corresponding to the times t_1 and t_2, and φ represents the *constant* final rotation, then

$$K = \frac{1}{t_2 - t_1} \log \left(\frac{\beta_1 - \varphi}{\beta_2 - \varphi} \right),$$

a formula which can readily be reconciled with the equation for a first-order reaction. The constant for the above 20% solution of sugar mixed with an equal volume of normal hydrochloric acid at 25° C. is 0.00205.

The acid is added for the purpose of accelerating the velocity of the reaction through the catalytic action of its hydrogen ions.

Catalysis of Methyl Acetate. — Another first-order reaction illustrating the catalytic action of hydrogen ions is the following:

$$CH_3 \cdot COOCH_3 + H_2O = CH_3COOH + CH_3 \cdot OH.$$

There is first prepared an approximately $\frac{N}{20}$ solution of barium hydroxide, and after this has been carefully standardized $\frac{N}{2}$ solutions of hydrochloric, nitric, and sulphuric acids are made up. A series of 25-c.c. bottles are then thoroughly cleaned and steamed, and each is furnished with a numbered or lettered paraffined stopper.

Each bottle is weighted with lead so that it can be wholly immersed in the thermostat. Into each bottle is introduced 20 c.c. of semi-normal acid and then the bottles are placed in the thermostat at 25°. When the contents of the bottles has acquired the temperature of the thermostat 1 c.c. of pure, dry methyl acetate is added and the mixture thoroughly shaken. Immediately after shaking 1 c.c. is removed and titrated with the $\frac{N}{20}$ barium hydroxide, the time being noted when the first drop of the barium hydroxide comes in contact with the solution. This is taken as the initial time of the reaction.

At intervals of twenty minutes for two hours, and then at longer intervals, other portions are removed and titrated, the bottles being kept continuously in the thermostat. A small residue, say 10 c.c., is kept at the constant temperature of 25° for three days and is then removed and titrated. This last titration gives the final reading for the solution.

If a_0 is the number of cubic centimetres of barium hydroxide initially required and a_1, $a_2 \ldots a_n$ the quantities required

at successive titrations, and A is the final quantity, which is a constant when equilibrium is attained, then

$$K = \log \frac{(A-a_0)-\log(A-a_n)}{t_n},$$

where t is the time expressed in minutes.

This formula also can be easily reconciled with the first-order reaction.

The constant $\frac{N}{2}$HCl and 1 c.c. of CH_3COOCH_3 is 0.0013 at 25°.

Reaction of the Second Order. — The equation for a second-order reaction is

$$\frac{dx}{dt} = K(a-x)^2,$$

which upon integration gives

$$K = \frac{1}{t} \cdot \frac{x}{a(a-x)}.$$

Saponification of Ethyl Acetate.—The reaction

$$CH_3COOC_2H_5 + \overset{+}{N}a,\overset{-}{O}H = CH_3\overset{-}{C}O\overset{-}{O},\overset{+}{N}a + C_2H_5OH$$

is a typical reaction of the second order.

To study this reaction we first prepare a $\frac{N}{20}$ solution of sodium hydroxide (free from carbonate), standardizing against succinic acid.

A $\frac{N}{20}$ aqueous solution of chemically pure, dry ethyl acetate is then prepared, the ester being weighed directly. The flasks or bottles containing these solutions are well stoppered and placed in the thermostat at 25° for several hours. When

the solutions have acquired the temperature of the thermostat 50 c.c. of each solution are introduced into a flask, previously warmed to 25°, and the mixture vigorously shaken. For the experiment 10 c.c. of the mixture is measured out and placed under a burette containing $\frac{N}{50}$ hydrochloric acid, phenolphthaleïn being added as an indicator. Four seconds before the initial time the stop-cock of the burette is opened and the acid allowed to flow in until within 10% of that required for neutralization. This requires approximately eight seconds. In the next ten seconds the exact quantity of acid required for neutralization can be determined. As an alternative an excess of acid may be run in at first and then titrated back with alkali afterward.

From the remainder of the mixture, successive portions are withdrawn and titrated in a similar manner at intervals of 5 minutes.

Finally 10 c.c. of the mixture is heated to 100° for thirty minutes, and when cool is titrated as above. This gives the excess of sodium hydroxide over the ester, when equilibrium has been attained. For equilibrium we have

$$K=\frac{\log a_t+\log (a_0-a_e)-\log a_0-\log (a_t-a_e)}{a_e t},$$

where a_0 is the number of cubic centimetres of hydrochloric acid required to neutralize the mixture initially, a_t is the quantity of acid required at any time t reckoned from the initial titration, and a_e is the number of cubic centimetres of acid required in the final titration.

TABLES.

I.

REDUCTION TO VACUUM OF WEIGHINGS MADE WITH BRASS WEIGHTS IN AIR.

s	k	s	k	s	k
0.7	+1.57	2.0	+0.457	8	+0.007
0.8	1.36	2.5	0.337	9	−0.010
0.9	1.19	3.0	0.257	10	−0.023
1.0	1.06	3.5	0.200	11	−0.034
1.1	0.95	4.0	0.157	12	−0.043
1.2	0.86	4.5	0.124	13	−0.051
1.3	0.78	5.0	0.097	14	−0.057
1.4	0.71	5.5	0.075	15	−0.063
1.5	0.66	6.0	0.057	16	−0.068
1.6	0.61	6.5	0.042	17	−0.072
1.7	0.56	7.0	0.029	18	−0.076
1.8	0.52	7.5	0.017	19	−0.080
1.9	0.49	8.0	0.007	20	−0.083
2.0	0.46			21	−0.086

II.

DENSITY.

Solids.

Aluminium	2.7	Lead	11.3
Brass	8.1–8.7	Nickel	8.8
Copper	8.5–8.9	Platinum	21.4
Glass, common	2.4–2.6	Quartz	2.65
" flint	3.0–5.9	Silver	10.5
Gold	19.3	Tin	7.3
Ice	0.9167	Zinc	7.1
Iridium	21.8–22.4	Wood, pine	0.35–0.50
Iron, cast	7.1–7.7	" oak	0.60–0.90
" wrought	7.8	" cork	0.2
" steel	7.8		

Liquids (20°).

Alcohol	0.789	Olive-oil	0.92
Amyl acetate	0.88	Petroleum	0.88
Carbon bisulphide	1.264	Turpentine	0.87
Chloroform	1.489	Water, pure	0.998
Ether	0.715	" sea	1.024
Glycerine	1.23	Mercury	13.546

Gases (0° and 760 mm.).

		Referred to Air = 1.	Referred to O = 16.
Air	0.001293	1.0000	14.477
Oxygen	0.001429	1.1052	16.000
Nitrogen	0.001251	0.9672	14.002
Hydrogen	0.0000899	0.06951	1.007
Carbon dioxide	0.001965	1.520	22.00
Electrolytic gas	0.000536	0.4148	6.00

III.

DENSITY OF WATER.

0°	0.999823	16°	0.998925
1	0.999882	17	0.998756
2	0.999923	18	0.998577
3	0.999947	19	0.998387
4	0.999955	20	0.998185
5	0.999947	21	0.997974
6	0.999923	22	0.997752
7	0.999884	23	0.997520
8	0.999831	24	0.997278
9	0.999763	25	0.997026
10	0.999682	26	0.996765
11	0.999587	27	0.996496
12	0.999480	28	0.996214
13	0.999359	29	0.995926
14	0.999226	30	0.995628
15	0.999081		

IV.

VOLUME OF WATER FROM 0° TO 31°.

0°	1.000126	16°	1.001025
1	1.000070	17	1.001193
2	1.000030	18	1.001373
3	1.000007	19	1.001564
4	1.000000	20	1.001768
5	1.000008	21	1.001981
6	1.000031	22	1.002204
7	1.000069	23	1.002438
8	1.000122	24	1.002681
9	1.000188	25	1.002935
10	1.000269	26	1.003199
11	1.000363	27	1.003472
12	1.000470	28	1.003788
13	1.000590	29	1.004045
14	1.000722	30	1.004346
15	1.000867	31	1.004656

V.

SURFACE TENSION OF LIQUIDS IN CONTACT WITH AIR.

Liquid.	Temp.	Surface Tension (Dynes per sq. cm.).
Acetone	14.0	25.6
Acetic acid	17.0	30.2
Amyl alcohol	15.0	24.8
Benzene	15.0	28.8
Carbon disulphide	20.0	30.5
Chloroform	20.0	28.3
Ether	20.0	18.4
Glycerine	17.0	63.14
Mercury	20.0	470.0
Methyl alcohol	15.0	24.7
Olive oil	20.0	34.7
Petroleum	20.0	25.9
Toluene	15.0	29.1
Turpentine	21.0	28.5

IV.

VISCOSITY OF LIQUIDS.

Liquid.	Temp.	Viscosity Coefficient.
Ammonia	14.5	0.0149
Glycerine	14.3	13.87
"	20.3	8.30
Mercury	20.0	0.0157
Olive oil	0	3.2653
Petroleum	17.5	0.0190
Rape-oil	20.0	1.63

VII.

REDUCTION OF GAS VOLUMES TO 0° AND 760 MM.

v = volume; s = density; t = temperature; H = pressure; $\alpha = 0.00367$.

$$v_0 = \frac{v}{1+\alpha t} \cdot \frac{H}{760}. \qquad s_0 = s(1+\alpha t)\frac{760}{H}.$$

	$1+\alpha t$	t	$1+\alpha t$	$\frac{H}{\text{mm.}}$	$\frac{H}{760}$
10	1.0367	21	1.0771	700	0.9211
11	1.0404	22	1.0807	710	0.9342
12	1.0440	23	1.0844	720	0.9474
13	1.0477	24	1.0881	730	0.9605
14	1.0514	25	1.0917	740	0.9737
15	1.0550	26	1.0954	750	0.9868
16	1.0587	27	1.0991	760	1.0000
17	1.0624	28	1.1028	770	1.0132
18	1.0661	29	1.1064	780	1.0263
19	1.0697	30	1.1101	790	1.0395
20	1.0734	99	1.3633	800	1.0526
		100	1.3670	810	1.0658
		101	1.3707	820	1.0789

VIII.

REDUCTION OF BAROMETER READINGS TO 0°.

When the height of the mercury column has been measured with a brass scale, the length of which is correct at 0°, the mercury and scale being at t°, the observed height is reduced to 0° by subtracting the value given in the table corresponding to the temperature and height.

	Observed Height in Centimetres.					
	72	73	74	75	76	77
10	0.12	0.12	0.12	0.12	0.12	0.12
11	0.13	0.13	0.13	0.13	0.14	0.14
12	0.14	0.14	0.14	0.15	0.15	0.15
13	0.15	0.15	0.16	0.16	0.16	0.16
14	0.16	0.17	0.17	0.17	0.17	0.17
15	0.17	0.18	0.18	0.18	0.18	0.19
16	0.19	0.19	0.19	0.19	0.20	0.20
17	0.20	0.20	0.20	0.21	0.21	0.21
18	0.21	0.21	0.22	0.22	0.22	0.22
19	0.22	0.22	0.23	0.23	0.23	0.24
20	0.23	0.24	0.24	0.24	0.25	0.25
21	0.25	0.25	0.25	0.25	0.26	0.26
22	0.26	0.26	0.26	0.27	0.27	0.27
23	0.27	0.27	0.28	0.28	0.28	0.29
24	0.28	0.28	0.29	0.29	0.29	0.30
25	0.29	0.30	0.30	0.30	0.31	0.31

IX.

REDUCTION OF MERCURY-IN-GLASS THERMOMETER READING TO THE NORMAL HYDROGEN SCALE.

FOR JENA NORMAL GLASS.

Reading.	Correction.	Reading.	Correction.
0°	0°.000	50°	−0°.109
10	−0 .055	60	−0 .096
20	−0 .090	70	−0 .076
30	−0 .109	80	−0 .053
40	−0 .115	90	−0 .027
50	−0 .109	100	0 .000

X.

CAPILLARY DEPRESSION OF MERCURY.

INTERPOLATED BY F. KOHLRAUSCH FROM MENDELEJEFF AND GUTKOWSKY.

Dia.	Height of Meniscus in mm.							
	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8
mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.
4	0.83	1.22	1.54	1.98	2.37			
5	0.47	0.65	0.86	1.19	1.45	1.80		
6	0.27	0.41	0.56	0.78	0.98	1.21	1.43	
7	0.18	0.28	0.40	0.53	0.67	0.82	0.97	1.13
8	.....	0.20	0.29	0.38	0.46	0.56	0.65	0.77
9	.....	0.15	0.21	0.28	0.33	0.40	0.46	0.52
10	.....	.....	0.15	0.20	0.25	0.29	0.33	0.37
11	.....	.....	0.10	0.14	0.18	0.21	0.24	0.27
12	.....	.....	0.07	0.10	0.13	0.15	0.18	0.19
13	....	.....	0.04	0.07	0.10	0.12	0.13	0.14

XI.

VAPOR PRESSURE OF WATER.

FROM −19° TO 100° IN MILLIMETRES OF MERCURY.

t.	*p.*	*Δ.*	*t.*	*p.*	*Δ.*	*t.*	*p.*	*Δ.*	*t.*	*p.*	*Δ.*
−19	1.029	0.091	+10	9.140	0.627	+40	54.87	3.00	+70	233.31	10.31
18	1.120	0.099	11	9.767	0.665	41	57.87	3.15	71	243.62	10.68
17	1.219	0.106	12	10.432	0.705	42	61.02	3.29	72	254.30	11.08
16	1.325	0.114	13	11.137	0.747	43	64.31	3.45	73	265.38	11.49
15	1.439	0.123	14	11.884	0.790	44	67.76	3.60	74	276.87	11.89
14	1.562	0.132	15	12.674	0.836	45	71.36	3.77	75	288.76	12.33
13	1.694	0.142	16	13.510	0.885	46	75.13	3.94	76	301.09	12.76
12	1.836	0.152	17	14.395	0.935	47	79.07	4.12	77	313.85	13.20
11	1.988		18	15.330	0.989	48	83.19	4.30	78	327.05	13.68
		0.163	19	16.319	1.044	49	87.49	4.49	79	340.73	14.18
−10	2.151	0.176	20	17.363	1.103	50	91.98	4.68	80	354.87	14.64
9	2.327	0.187	21	18.466	1.164	51	96.66	4.89	81	369.51	15.14
8	2.514	0.201	22	19.630	1.228	52	101.55	5.10	82	384.64	15.63
7	2.715	0.215	23	20.858	1.294	53	106.65	5.32	83	400.29	16.15
6	2.930	0.230	24	22.152	1.365	54	111.97	5.55	84	416.47	16.72
5	3.160	0.246	25	23.517	1.439	55	117.52	5.77	85	433.19	17.28
4	3.406	0.263	26	24.956	1.515	56	123.29	6.02	86	450.47	17.85
3	3.669	0.281	27	26.471	1.594	57	129.31	6.27	87	468.32	18.44
2	3.950	0.299	28	28.065	1.679	58	125.58	6.52	88	486.76	19.05
1	4.249		29	29.744	1.77	59	142.10	6.78	89	505.81	19.66
		0.320	30	31.51	1.86	60	148.88	7.07	90	525.47	20.30
0°	4.569	0.340	31	33.37	1.95	61	155.95	7.34	91	545.77	20.94
+ 1	4.909	0.363	32	35.32	2.05	62	163.29	7.63	92	566.71	21.62
2	5.272	0.386	33	37.37	2.15	63	170.02	7.94	93	588.83	22.31
3	5.658	0.411	34	39.52	2.26	64	178.86	8.24	94	610.64	23.02
4	6.069	0.438	35	41.78	2.38	65	187.10	8.57	95	633.66	23.74
5	6.507	0.465	36	44.16	2.49	66	195.67	8.89	96	657.40	24.48
6	6.972	0.494	37	46.65	2.61	67	204.56	9.23	97	681.88	25.25
7	7.466	0.525	38	49.26	2.74	68	213.79	9.58	98	707.13	26.03
8	7.991	0.557	39	52.00	2.87	69	223.37	9.94	99	733.16	26.84
9	8.548	0.592									

XII.

VAPOR PRESSURE OF MERCURY

IN MILLIMETRES, ACCORDING TO REGNAULT AND HERTZ (*a*) AND RAMSAY AND YOUNG (*b*).

	a.	*b.*		*a.*	*b.*		*a.*	*b.*		*a.*	*b.*
0°	0.0002	.....	100°	0.285	0.270	200°	18.25	17.02	300°	242.2	246.8
10	0.0005	.....	110	0.470	.....	210	25.12	.....	310	299.7	304.8
20	0.0013	.....	120	0.779	0.719	220	34.9	31.96	320	368.7	373.7
30	0.0029	.....	130	1.24	.....	230	45.4	.....	330	450.9	454.4
40	0.007	0.008	140	1.93	1.763	240	58.8	.....	340	548.4	548.6
50	0.014	0.015	150	2.93	.....	250	75.8	.....	350	663.2	658.0
60	0.028	0.029	160	4.38	4.013	260	96.7	.....	360	797.7	.....
70	0.051	0.052	170	6.41	.....	270	123.0	123.9	370	954.7	.....
80	0.093	0.093	180	9.23	8.535	280	155.2	157.4	380	1139.7	.....
90	0.163	0.160	190	13.07	.....	290	194.5	198.0	390	1346.7	.....

XIII.

TABLE FOR THE CONVERSION OF THERMOMETER READINGS.

Degrees Centigrade $\times 1.8 + 32$ = degrees Fahrenheit.

$$\frac{\text{Degrees Fahrenheit} - 32}{1.8} = \text{degrees Centigrade.}$$

$$\frac{\text{Degrees Réaumur} \times 9}{4} + 32 = \text{degrees Fahrenheit.}$$

$$\frac{\text{Degrees (Fahrenheit} - 32) 4}{9} = \text{degrees Réaumur.}$$

$$\frac{\text{Degrees Réaumur} \times 5}{4} = \text{degrees Centigrade.}$$

$$\frac{\text{Degrees Centigrade} \times 4}{5} = \text{degrees Réaumur.}$$

XIV.

SPECIFIC HEATS, HEATS OF FUSION, AND MELTING-POINTS OF THE ELEMENTS.

Name.	Specific Heat.	Heat of Fusion.	Melting-point, Centigrade	Authority for Melting-points.
Aluminium	0.222	80	625	Roberts-Austin
Antimony	.051	16	432	Pouillet
Bismuth	.031	12.4	268.3	Rudberg
Cadmium	.055	13.1	320.7	Person
Chromium	.100	.....	1515	E. A. Lewis
Cobalt	.107	68	1500	Pictet
Copper	.095	43	1054	Violle
Gold	.032	16.3	1045	Violle
Iridium	.033	28	1950	Violle
Iron, wrought	.112	69	1600	Pictet
Lead	.032	5.4	326.2	Person
Magnesium	.245	58	750	
Manganese	.122	.....	1245	Heræus
Mercury	.032	2.8	−39.5	Regnault
Nickel	.108	68	1484	Bredig
Osmium	.031	35	2500	Pictet
Palladium	.059	36.3	1587	Bredig
Platinum	.032	27.2	1780	Bredig
Rhodium	.058	52	2000	Pictet
Ruthenium	.061	46	2000+	Deville & Debray
Silver	.057	24.7	961.5	Bredig
Tin	.056	14.5	232.7	Person
Titanium	.113	.....	3000	
Tungsten	.035	.....	1700	
Zinc	.096	22.6	419	Bredig

XV.

COEFFICIENTS OF EXPANSION, SPECIFIC HEATS, MELTING-POINTS, AND BOILING-POINTS OF LIQUIDS.

	Coefficient of Expansion.	Specific Heat.	Melting-point.	Boiling-point.
Ether	0.00163	0.54	−118°	34°.9
Alcohol	0.00110	0.58	−110	78 .3
Amyl alcohol	0.00093	0.55	.....	130 .0
Aniline	0.00085	0.49	− 8	184 .0
Benzene	0.00024	0.40	+ 5	80 .3
Chloroform	0.00026	0.23	− 70	61 .2
Acetic acid	0.00007	0.50	+ 17	118 .0
Glycerine	0.00050	0.58	− 20	290 .0
Methyl alcohol	0.00022	0.60	.....	66 .0
Nitrobenzene	0.00085	0.34	+ 3	210 .0
Phenol	0.00084	....	+ 40	183 .0
Toluene	0.00109	0.40	−102	110 .0
Water	0.00018	1	0	100 .0
Xylene	0.00101	0.40	+ 15	140 .0

XVI.

BOILING TEMPERATURE t OF WATER AT BAROMETRIC PRESSURE b.

$\frac{b}{\text{cm.}}$	$\frac{t}{°}$	$\frac{b}{\text{cm.}}$	$\frac{t}{°}$	$\frac{b}{\text{cm.}}$	$\frac{t}{°}$
72.0	98.49	74.0	99.26	76.0	**100**
72.1	98.53	74.1	99.29	76.1	100.04
72.2	98.57	74.2	99.33	76.2	100.07
72.3	98.61	74.3	99.37	76.3	100.11
72.4	98.65	74.4	99.41	76.4	100.15
72.5	98.69	74.5	99.44	76.5	100.18
72.6	98.72	74.6	99.48	76.6	100.22
72.7	98.76	74.7	99.52	76.7	100.26
72.8	98.80	74.8	99.55	76.8	100.29
72.9	98.84	74.9	99.59	76.9	100.33
73.0	98.88	75.0	99.63	77.0	100.37
73.1	98.92	75.1	99.67	77.1	100.40
73.2	98.95	75.2	99.70	77.2	100.44
73.3	98.99	75.3	99.74	77.3	100.48
73.4	99.03	75.4	99.78	77.4	100.51
73.5	99.07	75.5	99.82	77.5	100.55
73.6	99.10	75.6	99.85	77.6	100.58
73.7	99.14	75.7	99.89	77.7	100.62
73.8	99.18	75.8	99.93	77.8	100.66
73.9	99.22	75.9	99.96	77.9	100.69

XVII.

CORRECTION FOR TEMPERATURE OF MERCURY IN THERMOMETER-STEM.

n	$t-t'$									
	70°	80°	90°	100°	120°	140°	160°	180°	200°	220°
10°	0.02	0.03	0.05	0.07	0.11	0.17	0.21	0.27	0.33	0.38
20	0.13	0.15	0.18	0.22	0.29	0.38	0.46	0.53	0.61	0.67
30	0.24	0.28	0.33	0.39	0.48	0.59	0.70	0.78	0.88	0.97
40	0.35	0.41	0.48	0.56	0.68	0.82	0.94	1.04	1.16	1.28
50	0.47	0.53	0.62	0.72	0.88	1.03	1.17	1.31	1.44	1.59
60	0.57	0.66	0.77	0.89	1.09	1.25	1.42	1.58	1.74	1 90
70	0.69	0.79	0.92	1.06	1.30	1.47	1.67	1.86	2.04	2.23
80	0.80	0.91	1.05	1.21	1.52	1.71	1.94	2.15	2.33	2.55
90	0.91	1.04	1.19	1.38	1.73	1.96	2.20	2.42	2.64	2.89
100	1.02	1.18	1.35	1.56	1.97	2.18	2.45	2.70	2.94	3.23
110	.....	.....	.....	1.78	2.19	2.43	2.70	2.98	3.26	3.57
120	.....	.....	.....	1.98	2.43	2.69	2.95	3.26	3.58	3.92
130	.....	.....	.....	.....	2.68	2.94	3.20	3.56	3.89	4.28
140	.....	.....	.....	.....	2.92	3.22	3.47	3.86	4.22	4.64
150	.....	.....	.....	.....	.....	.....	3.74	4.15	4.56	5.01
160	.....	.....	.....	.....	.....	.....	4.00	4.46	4.90	5.39
170	.....	.....	.....	.....	.....	.....	4.27	4.76	5.24	5.77
180	.....	.....	.....	.....	.....	.....	4.54	5.07	5.59	6.15
190	.....	.....	.....	.....	.....	.....	.....	5.38	5.95	6.54
200	.....	.....	.....	.....	.....	....	.....	5.70	6.30	6.94
210	.....	.....	.....	.....	.....	.....	.....	.....	6 68	7.35
220	.....	.....	.....	.....	.....	.....	.....	.....	7.04	7.75

XVIII.

WAVE-LENGTHS OF LINES OF SOLAR SPECTRUM IN AIR AT 18°

PRESSURE 760 MM. UNIT = MICRON = 0.001 MM.

Line.	Element.	Wave-length μ	Line.	Element.	Wave-length μ
A	....	0.76280	*c*	Fe	0.49576
a	....	0.71850	*F*	H	0.48614
B	O	0.68701	*d*	Fe	0.46682
C	H	0.65629	*e*	Fe	0.43836
α	O	0.62781	*f*	H	0.43405
D_1	Na	0.58960	*G*	Fe,Ca	0.43079
D_2	Na	0.58900	*h*	H	0.41018
E	Fe,Ca	0.52703	*H*	H,Ca	0.39685
b_1	Mg	0.51837	*K*	Ca	0.39337

XIX.

TABLE FOR WHEATSTONE'S BRIDGE.

$\frac{a}{1-a}$ from $a=0.001$ to 0.999.

a	0	1	2	3	4	5	6	7	8	9
00	0.0000	0010	0020	0030	0040	0050	0060	0071	0081	0091
01	0101	0111	0122	0132	0142	0152	0163	0173	0183	0194
02	0204	0215	0225	0235	0246	0256	0267	0278	0288	0299
03	0309	0320	0331	0341	0353	0363	0373	0384	0395	0406
04	0417	0428	0438	0449	0460	0471	0482	0493	0504	0515
05	0526	0537	0549	0560	0571	0582	0593	0605	0616	0627
06	0638	0650	0661	0672	0684	0695	0707	0718	0730	0741
07	0753	0764	0776	0788	0799	0811	0823	0834	0846	0858
08	0870	0881	0893	0905	0917	0929	0941	0953	0965	0977
09	0989	1001	1013	1025	1038	1050	1062	1074	1087	1099
10	0.1111	1124	1136	1148	1161	1173	1186	1198	1211	1223
11	1236	1249	1261	1274	1287	1299	1312	1325	1338	1351
12	1364	1377	1390	1403	1416	1429	1442	1455	1468	1481
13	1494	1508	1521	1534	1547	1561	1574	1588	1601	1614
14	1628	1641	1655	1669	1682	1696	1710	1723	1737	1751
15	1765	1779	1793	1806	1820	1834	1848	1862	1877	1891
16	1905	1919	1933	1947	1962	1976	1990	2005	2019	2034
17	0.2048	2063	2077	2092	2107	2121	2136	2151	2166	2180
18	2195	2210	2225	2240	2255	2270	2285	2300	2315	2331
19	2346	2361	2376	2392	2407	2422	2438	2453	2469	2484
20	2500	2516	2531	2547	2563	2579	2595	2610	2626	2642
21	2658	2674	2690	2707	2723	2739	2755	2771	2788	2804
22	2821	2837	2854	2870	2887	2903	2920	2937	2953	2970
23	2987	3004	3021	3038	3055	3072	3089	3106	3123	3141
24	0.3158	3175	3193	3210	3228	3245	3263	3280	3298	3316
25	3333	3351	3369	3387	3405	3423	3441	3459	3477	3495
26	3514	3532	3550	3569	3587	3605	3624	3643	3661	3680
27	3699	3717	3736	3755	3774	3793	3812	3831	3850	3870
28	3889	3908	3928	3947	3967	3986	4006	4025	4045	4065
29	0.4085	4104	4124	4144	4164	4184	4205	4225	4245	4265

XIX—(*Continued.*)

TABLE FOR WHEATSTONE'S BRIDGE.

a	0	1	2	3	4	5	6	7	8	9
30	4286	4306	4327	4347	4368	4389	4409	4430	4451	4472
31	4493	4514	4535	4556	4577	4599	4620	4641	4663	4684
32	4706	4728	4749	4771	4793	4815	4837	4859	4881	4903
33	4925	4948	4970	4993	5015	5038	5060	5083	5106	5129
34	0.5152	5175	5198	5221	5244	5267	5291	5314	5337	5361
35	5385	5408	5432	5456	5480	5504	5528	5552	5576	5601
36	5625	5650	5674	5699	5723	5748	5773	5798	5823	5848
37	5873	5898	5924	5949	5974	6000	6026	6051	6077	6103
38	0.6129	6155	6181	6208	6234	6260	6287	6313	6340	6367
39	6393	6420	6447	6475	6502	6529	6556	6584	6611	6639
40	6667	6695	6722	6750	6779	6807	6835	6863	6892	6921
41	6949	6978	7007	7036	7065	7094	7123	7153	7182	7212
42	0.7241	7271	7301	7331	7361	7391	7422	7452	7483	7513
43	7544	7575	7606	7637	7668	7699	7731	7762	7794	7825
44	7857	7889	7921	7953	7986	8018	8051	8083	8116	8149
45	0.8182	8215	8248	8282	8315	8349	8382	8416	8450	8484
46	8519	8553	8587	8622	8657	8692	8727	8762	8797	8832
47	8868	8904	8939	8975	9011	9048	9084	9121	9157	9194
48	0.9231	9268	9305	9342	9380	9418	9455	9493	9531	9570
49	9608	9646	9685	9724	9763	9802	9841	9881	9920	9960
50	1.000	1.004	1.008	1.012	1.016	1.020	1.024	1.028	1.033	1.037
51	1.041	1.045	1.049	1.053	1.058	1.062	1.066	1.070	1.075	1.079
52	1.083	1.088	1.092	1.096	1.101	1.105	1.110	1.114	1.119	1.123
53	1.128	1.132	1.137	1.141	1.146	1.151	1.155	1.160	1.165	1.169
54	1.174	1.179	1.183	1.188	1.193	1.198	1.203	1.208	1.212	1.217
55	1.222	1.227	1.232	1.237	1.242	1.247	1.252	1.257	1.262	1.268
56	1.273	1.278	1.283	1.288	1.294	1.299	1.304	1.309	1.315	1.320
57	1.326	1.331	1.336	1.342	1.347	1.353	1.358	1.364	1.370	1.375
58	1.381	1.387	1.392	1.398	1.404	1.410	1.415	1.421	1.427	1.433
59	1.439	1.445	1.451	1.457	1.463	1.469	1.475	1.481	1.488	1.494
60	1.500	1.506	1.513	1.519	1.525	1.532	1.538	1.545	1.551	1.558
61	1.564	1.571	1.577	1.584	1.591	1.597	1.604	1.611	1.618	1.625
62	1.632	1.639	1.646	1.653	1.660	1.667	1.674	1.681	1.688	1.695
63	1.703	1.710	1.717	1.725	1.732	1.740	1.747	1.755	1.762	1.770
64	1.778	1.786	1.793	1.801	1.809	1.817	1.825	1.833	1.841	1.849

XIX—(*Continued.*)

TABLE FOR WHEATSTONE'S BRIDGE.

a	0	1	2	3	4	5	6	7	8	*v*
65	1.857	1.865	1.874	1.882	1.890	1.899	1.907	1.915	1.924	1.933
66	1.941	1.950	1.959	1.967	1.976	1.985	1.994	2.003	2.012	2.021
67	2.030	2.040	2.049	2.058	2.067	2.077	2.086	2.096	2.106	2.115
68	2.125	2.135	2.145	2.155	2.165	2.175	2.185	2.195	2.205	2.215
69	2.226	2.236	2.247	2.257	2.268	2.279	2.289	2.300	2.311	2.322
70	2.333	2.344	2.356	2.367	2.378	2.390	2.401	2.413	2.425	2.436
71	2.448	2.460	2.472	2.484	2.497	2.509	2.521	2.534	2.546	2.559
72	2.571	2.584	2.597	2.610	2.623	2.636	2.650	2.663	2.676	2.690
73	2.704	2.717	2.731	2.745	2.759	2.774	2.788	2.802	2.817	2.831
74	2.846	2.861	2.876	2.891	2.906	2.922	2.937	2.953	2.968	2.984
75	3.000	3.016	3.032	3.049	3.065	3.082	3.098	3.115	3.132	3.149
76	3.167	3.184	3.202	3.219	3.237	3.255	3.274	3.292	3.310	3.329
77	3.348	3.367	3.386	3.405	3.425	3.444	3.464	3.484	3.505	3.525
78	3.545	3.566	3.587	3.608	3.630	3.651	3.673	3.695	3.717	3.739
79	3.762	3.785	3.808	3.831	3.854	3.878	3.902	3.926	3.950	3.975
80	4.000	4.025	4.051	4.076	4.102	4.128	4.155	4.181	4.208	4.236
81	4.263	4.291	4.319	4.348	4.376	4.405	4.435	4.465	4.495	4.525
82	4.556	4.587	4.618	4.650	4.682	4.714	4.747	4.780	4.814	4.848
83	4.882	4.917	4.952	4.988	5.024	5.061	5.098	5.135	5.173	5.211
84	5.250	5.289	5.329	5.369	5.410	5.452	5.494	5.536	5.579	5.623
85	5.667	5.711	5.757	5.803	5.849	5.897	5.944	5.993	6.042	6.092
86	6.143	6.194	6.246	6.299	6.353	6.407	6.463	6.519	6.576	6.634
87	6.692	6.752	6.813	6.874	6.937	7.000	7.065	7.130	7.197	7.264
88	7.333	7.403	7.475	7.547	7.621	7.696	7.772	7.850	7.929	8.009
89	8.091	8.174	8.259	8.346	8.434	8.524	8.615	8.709	8.804	8.901
90	9.000	9.101	9.204	9.309	9.417	9.526	9.638	9.753	9.870	9.989
91	10.11	10.33	10.36	10.49	10.63	10.77	10.90	11.05	11.20	11.35
92	11.50	11.66	11.82	11.99	12.16	12.33	12.51	12.70	12.89	13.08
93	13.29	13.49	13.71	13.93	14.15	14.38	14.63	14.87	15.13	15.39
94	15.67	15.95	16.24	16.54	16.86	17.18	17.52	17.87	18.23	18.61
95	19.00	19.41	19.83	20.28	20.74	21.22	21.73	22.26	22.81	23.39
96	24.00	24.64	25.32	26.03	26.78	27.57	28.41	29.30	30.25	31.26
97	32.33	33.48	34.71	36.04	37.46	39.00	40.67	42.48	44.45	46.62
98	49.00	51.6	54.6	57.8	61.5	65.7	70.4	75.9	82.3	89.9
99	99.0	110	124	142	163	199	249	332	499	999

XX.

TABLE OF INTERNATIONAL ATOMIC WEIGHTS.

Name.	Sym.	O=16.	H=1.	Name.	Sym.	O=16.	H=1.
Aluminium	Al	27.1	26.9	Molybdenum	Mo	96.0	95.3
Antimony	Sb	120.2	119.3	Neodymium	Ne	143.6	142.5
Argon	A	39.9	39.6	Neon	....	20	19.9
Arsenic	As	75.0	74.4	Nickel	Ni	58.7	58.3
Barium	Ba	137.4	136.4	Nitrogen	N	14.04	13.93
Bismuth	Bi	208.5	206.9	Osmium	Os	191	189.6
Boron	B	11	10.9	Oxygen	O	16.00	15.88
Bromine	Br	79.96	79.36	Palladium	Pd	106.5	105.7
Cadmium	Cd	112.4	111.6	Phosphorus	P	31.0	30.77
Cæsium	Cs	133	132	Platinum	Pt	194.8	193.3
Calcium	Ca	40.1	39.8	Potassium	K	39.15	38.86
Carbon	C	12.00	11.91	Praseodymium	Pr	140.5	139.4
Cerium	Ce	140	139	Radium	Ra	225	223.3
Chlorine	Cl	35.45	35.18	Rhodium	Rh	103.0	102.2
Chromium	Cr	52.1	51.7	Rubidium	Rb	85.4	84.8
Cobalt	Co	59.0	58.56	Ruthenium	Ru	101.7	100.9
Columbium (Niobium)	Cb	94	93.3	Samarium	Sm	150	148.9
Copper	Cu	63.6	63.1	Scandium	Sc	44.1	43.8
Erbium	E	166	164.8	Selenium	Se	79.2	78.6
Fluorine	F	19	18.9	Silicon	Si	28.4	28.2
Gadolinium	Gd	156	155	Silver	Ag	107.93	107.12
Gallium	Ga	70	69.5	Sodium	Na	23.05	22.88
Germanium	Ge	72.5	71.9	Strontium	Sr	87.6	86.94
Glucinum (Beryllium)	Gl	9.1	9.03	Sulphur	S	32.06	31.83
Gold	Au	197.2	195.7	Tantalum	Ta	183	181.6
Helium	He	4	4	Tellurium	Te	127.6	126.6
Hydrogen	H	1.008	1.000	Terbium	Tb	160	158.8
Indium	In	114	113.1	Thallium	Tl	204.1	202.6
Iodine	I	126.85	125.90	Thorium	Th	232.5	230.8
Iridium	Ir	193.0	191.5	Thulium	Tm	171	169.7
Iron	Fe	55.9	55.5	Tin	Sn	119.0	118.1
Krypton	K	81.8	81.2	Titanium	Ti	48.1	47.7
Lanthanum	La	138.9	137.9	Tungsten	W	184.0	182.6
Lead	Pb	206.9	205.35	Uranium	U	238.5	236.7
Lithium	Li	7.03	6.98	Vanadium	V	51.2	50.8
Magnesium	Mg	24.36	24.18	Xenon	X	128	127
Manganese	Mn	55.0	54.6	Ytterbium	Yb	173.0	171.7
Mercury	Hg	200.0	198.5	Yttrium	Yt	89.0	88.3
				Zinc	Zn	65.4	64.9
				Zirconium	Zr	90.6	89.9

XXI.
LOGARITHMS OF NUMBERS.

	0	1	2	3	4	5	6	7	8	9	Diff.
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	42
11	414	453	492	531	569	607	645	682	719	755	38
12	792	828	864	899	934	969	1004	1038	1072	1106	35
13	1139	1173	1206	1239	1271	1303	335	367	399	430	32
14	461	492	523	553	584	614	644	673	703	732	30
15	761	790	818	847	875	903	931	959	987	2014	28
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	279	26
17	304	330	355	380	405	430	455	480	504	529	25
18	553	577	601	625	648	672	695	718	742	765	24
19	788	810	833	856	878	900	923	945	967	989	22
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	21
21	222	243	263	284	304	324	345	365	385	404	20
22	424	444	464	483	502	522	541	560	579	598	19
23	617	636	655	674	692	711	729	747	766	784	
24	802	820	838	856	874	892	909	927	945	962	18
25	979	997	4014	4031	4048	4065	4082	4099	4116	4133	17
26	4150	4166	183	200	216	232	249	265	281	298	16
27	314	330	346	362	378	393	409	425	440	456	
28	472	487	502	518	533	548	564	579	594	609	15
29	624	639	654	669	683	698	713	728	742	757	
30	771	786	800	814	829	843	857	871	886	900	14
31	914	928	942	955	969	983	997	5011	5024	5038	
32	5051	5065	5079	5092	5105	5119	5132	145	159	172	13
33	185	198	211	224	237	250	263	276	289	302	
34	315	328	340	353	366	378	391	403	416	428	
35	441	453	465	478	490	502	515	527	539	551	12
36	563	575	587	599	611	623	635	647	658	670	
37	682	694	705	717	729	740	752	763	775	786	
38	798	809	821	832	843	855	866	877	888	899	
39	911	922	933	944	955	966	977	988	999	6010	11
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	117	
41	128	138	149	159	170	180	191	201	212	222	
42	232	243	253	263	274	284	294	304	314	325	
43	335	345	355	365	375	385	395	405	415	425	10
44	435	444	454	464	474	484	493	503	513	522	
45	532	542	551	561	571	580	590	599	609	618	
46	628	637	646	656	665	675	684	693	702	712	
47	721	730	739	749	758	767	776	785	794	803	
48	812	821	830	839	848	857	866	875	884	893	9
49	902	911	920	928	937	946	955	964	972	981	
50	990	998	7007	7016	7024	7033	7042	7050	7059	7067	
51	7076	7084	093	101	110	118	126	135	143	152	
52	160	168	177	185	193	202	210	218	226	235	
53	243	251	259	267	275	284	292	300	308	316	8
54	324	332	340	348	356	364	372	380	388	396	
	0	1	2	3	4	5	6	7	8	9	

LOGARITHMS OF NUMBERS—(*Continued*).

	0	1	2	3	4	5	6	7	8	9	Diff.
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	8
56	482	490	497	505	513	520	528	536	543	551	
57	559	566	574	582	589	597	604	612	619	627	
58	634	642	649	657	664	672	679	686	694	701	
59	709	716	723	731	738	745	752	760	767	774	
60	782	789	796	803	810	818	825	832	839	846	
61	853	860	868	875	882	889	896	903	910	917	7
62	924	931	938	945	952	959	966	973	980	987	
63	993	8000	8007	8014	8021	8028	8035	8041	8048	8055	
64	8062	069	075	082	089	096	102	109	116	122	
65	129	136	142	149	156	162	169	176	182	189	
66	195	202	209	215	222	228	235	241	248	254	
67	261	267	274	280	287	293	299	306	312	319	
68	325	331	338	344	351	357	363	370	376	382	
69	388	395	401	407	414	420	426	432	439	445	
70	451	457	463	470	476	482	488	494	500	506	
71	513	519	525	531	537	543	549	555	561	567	6
72	573	579	585	591	597	603	609	615	621	627	
73	633	639	645	651	657	663	669	675	681	686	
74	692	698	704	710	716	722	727	733	739	745	
75	751	756	762	768	774	779	785	791	797	802	
76	808	814	820	825	831	837	842	848	854	859	
77	865	871	876	882	887	893	899	904	910	915	
78	921	927	932	938	943	949	954	960	965	971	
79	976	982	987	993	998	9004	9009	9015	9020	9025	
80	9031	9036	9042	9047	9053	058	063	069	074	079	
81	085	090	096	101	106	112	117	122	128	133	
82	138	143	149	154	159	165	170	175	180	186	
83	191	196	201	206	212	217	222	227	232	238	
84	243	248	253	258	263	269	274	279	284	289	
85	294	299	304	309	315	320	325	330	335	340	
86	345	350	355	360	365	370	375	380	385	390	5
87	395	400	405	410	415	420	425	430	435	440	
88	445	450	455	460	465	469	474	479	484	489	
89	494	499	504	509	513	518	523	528	533	538	
90	542	547	552	557	562	566	571	576	581	586	
91	590	595	600	605	609	614	619	624	628	633	
92	638	643	647	652	657	661	666	671	675	680	
93	685	689	694	699	703	708	713	717	722	727	
94	731	736	741	745	750	754	759	763	768	773	
95	777	782	786	791	795	800	805	809	814	818	
96	823	827	832	836	841	845	850	854	859	863	
97	868	872	877	881	886	890	894	899	903	908	
98	912	917	921	926	930	934	939	943	948	952	
99	956	961	965	969	974	978	983	987	991	996	4
	0	1	2	3	4	5	6	7	8	9	

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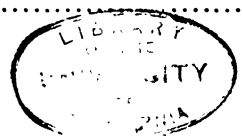

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